New Syntheses of Aromatic Acid Chlorides from Trichloromethylarenes. 1. Reaction with Sulfur Dioxide

Christian S. Rondestvedt, Jr.

Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware 19898

Received April 27, 1976

Trichloromethylarenes (benzotrichlorides) react with sulfur dioxide above ~150 °C to yield aroyl chloride and thionyl chloride in high yields. 1,3-Bis(trichloromethyl)benzene reacts especially well to yield isophthaloyl chloride. The reaction proceeds at a much lower temperature in the presence of antimony pentachloride or other Lewis acids, although Friedel–Crafts side reactions reduce the yield of aroyl chloride unless the ring bears strongly electron-attracting substituents. Both thermal and catalyzed reactions are interpreted in terms of a dichlorobenzyl cation intermediate, although an alternative radical mechanism was also demonstrated by adding di-*tert*-butyl peroxide.

Laboratory synthesis of acid chlorides is readily achieved by treating the acid with thionyl chloride, phosphorus pentachloride, or other inorganic nonmetal halide, often with a little dimethylformamide or tertiary amine as catalyst. Industrial synthesis is similar, except that phosgene is usually the reagent of choice because of its low cost.[1]

Aromatic acids are often prepared by oxidation of methylarenes. One useful oxidant is chlorine, and some acids have been prepared commercially by side-chain chlorination of the methylarene, followed by hydrolysis. Where the acid chloride is desired, hydrolysis can be controlled, for the acid chloride is hydrolyzed more slowly *under acidic conditions* than is the trichloromethyl group. Alcohols and carboxylic acids react similarly, with Lewis acid catalysis, to yield alkyl chlorides and other acid chlorides, respectively.

$$\mathrm{ArCH_3 + 3Cl_2 \dashrightarrow ArCCl_3 + 3HCl} \qquad (1)$$

$$\mathrm{ArCCl_3 + H_2O \dashrightarrow ArCOCl + 2HCl} \qquad (2)^{2}$$

$$\mathrm{ArCCl_3 + ROH \dashrightarrow ArCOCl + RCl + HCl} \qquad (3)^{3}$$

$$\mathrm{ArCCl_3 + RCOOH \dashrightarrow ArCOCl + RCOCl + HCl} \qquad (4)^{4}$$

Less well known are the reactions of trichloromethylarenes with metal oxides. Schreyer reported that *pure* titanium dioxide or vanadium pentoxide (*free from iron or aluminum oxides,* hence not the naturally occurring materials) react readily with hexachloro-*p*-xylene (or the meta isomer) to yield titanium tetrachloride or vanadium oxytrichloride, along with terephthaloyl (or isophthaloyl) chloride.[5] Closely related is the tested synthesis of anhydrous metal chlorides from metal oxides and hexachloropropene.[6]

$$\mathrm{2ArCCl_3 + TiO_2 \dashrightarrow 2ArCOCl + TiCl_4} \qquad (5)$$

$$n\mathrm{CCl_2{=}CClCCl_3} + \mathrm{M_2O}_n \dashrightarrow n\mathrm{CCl_2{=}CClCOCl} + 2\mathrm{MCl}_n \qquad (6)$$

The present research was directed at economical synthesis of isophthaloyl and terephthaloyl chlorides which are currently prepared from *m*- or *p*-xylene by air oxidation, followed by phosgenation. Attention was focused on the side-chain chlorination of the xylene, followed by transformation of the trichloromethyl groups to carbonyl chloride. Water (eq 2) is unsurpassed as an economical reagent, but it produces 2 mol of hydrogen chloride by-product per trichloromethyl group. The metal oxide reaction does not produce hydrogen chloride but rather a potentially saleable metal chloride.

In this work, we sought nonmetal oxides because many anhydrous metal chlorides are Lewis acids which can cause Friedel–Crafts or other undesirable side reactions.[5] The fundamental chemistry involves transfer of oxygen from the inorganic element (E) to the carbon of the trichloromethyl group, with movement of two chlorines from that carbon to the inorganic element.

$$\mathrm{ArCCl_3} + \mathrm{E_2O}_n \dashrightarrow \mathrm{ArCOCl} + \mathrm{E_2O}_{n-1}\mathrm{Cl_2} \qquad (7)$$

Consideration of the bond energies involved in eq 7 directed attention to the elements from silicon to chlorine; cost and availability factors pinpointed sulfur oxides. Other nonmetal oxides are discussed in the following paper.

Results and Discussion

$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-Hexachloro-*m*-xylene (HCMX)[7] was selected for most of this study because it is readily prepared from *m*-xylene by photo- or peroxide-initiated chlorination. Other trichloromethylarenes were studied less intensively. In the first experiment, HCMX was sealed in an autoclave with 3 mol of sulfur dioxide and heated stepwise until a pressure drop at about 200 °C showed that reaction had set in. After the pressure had become constant, the vessel contained isophthaloyl chloride (IPC) and thionyl chloride in addition to incompletely converted reagents.

$$\underset{\text{HCMX}}{m\text{-}\mathrm{C_6H_4(CCl_3)_2}} + \mathrm{SO_2} \dashrightarrow \underset{\text{TCTC}}{m\text{-}\mathrm{C_6H_4(CCl_3)COCl}} + \mathrm{SOCl_2} \qquad (8)$$

$$m\text{-}\mathrm{C_6H_4(CCl_3)COCl} + \mathrm{SO_2} \dashrightarrow \underset{\text{IPC}}{m\text{-}\mathrm{C_6H_4(COCl)_2}} + \mathrm{SOCl_2} \qquad (9)$$

Detailed study showed that time, temperature, and especially sulfur dioxide pressure determined high conversion and yield. HCMX should react only with *dissolved* sulfur dioxide, and its solubility should vary directly with pressure and inversely with temperature. Above about 220 °C with a given mole ratio, conversions decrease with increasing temperature; compare entries 3, 4, 8, and 11 in Table I, which lists selected examples. High sulfur dioxide ratios give higher pressures and solubilities, and faster reactions. The most productive way of increasing conversion without using a large excess of sulfur dioxide is by operating with the autoclave nearly full so that the final pressure exceeds about 1000 psi.

Thionyl chloride increases the rate. HCMX and 1 mol of thionyl chloride reacted faster with sulfur dioxide than did HCMX alone. When incompletely converted organic material was distilled and then treated with fresh sulfur dioxide, the reaction was quite slow compared to runs in which the same amount of additional sulfur dioxide was added to the total crude product containing thionyl chloride. Thionyl chloride probably enhances the solubility of sulfur dioxide.

The first trichloromethyl group in HCMX reacts faster than the second. For example, in one run carried partially to completion, the product contained about 50% of trichloro-*m*-toluyl chloride (TCTC), 20% of IPC, and 30% of HCMX. At higher conversions, HCMX disappeared completely before TCTC. At 20% conversion, only 3% of IPC was formed. Pure TCTC gave lower conversions than did HCMX under the same conditions.

Table I. Reaction of m-$C_6H_4(CCl_3)_2$ (HCMX) with Sulfur Dioxide (Uncatalyzed)[a]

HCMX, mol	SO_2/HCMX mole ratio	Temp, °C	Time,[b] h	Press. range, psig	$SOCl_2$,[c] %	IPC,[d] %	Purity,[e] %
0.2	2.5	222	5.5	950–525	90	94	
0.2	2.5	190	10.0	800–725	37		
0.2	3.0	300	2.0		68	96	63
0.2	3.0	330	1.0		29	115	22[f]
0.5	2.6	250	2.0	1590–1000	91	97	95
0.2	3.5	230	2.0	630–510	86	93	99
0.2	5.0	230	2.0	500–490	84	96	98
0.5	3.0	230	3.0		90	96	99
0.5[g]	2.6	235	3.0	2600–1080	78	91g	99
0.2	7.5	150	10.0		28		31[f]
0.2	2.5	230	2.0		90	95	98

[a] Run by the procedure in the Experimental Section. [b] Hours at reaction temperature, excluding heating and cooling times. [c] Based on 2 mol of $SOCl_2$ per mole of HCMX. If the HCMX contains no $ArCHCl_2$, the $SOCl_2$ is pure. If it contains $ArCHCl_2$, S_2Cl_2 is also formed. See part 3. [d] Weight of once-distilled product divided by theoretical weight, calculated as pure isophthaloyl chloride. A yield over 100% betokens incomplete conversion. [e] Determined by GC as described in the Experimental Section. Except as noted, the sole significant impurity is trichloro-*m*-toluyl chloride. [f] Product contained a substantial amount of HCMX as well. [g] Starting with hexachloro-*p*-xylene, the product was terephthaloyl chloride.

Table II. Reaction of m-$C_6H_4(CCl_3)_2$ (HCMX) with Sulfur Dioxide (Catalyzed)[a,b]

HCMX, mol	SO_2/HCMX, mole ratio	Catalyst (mol %)	Temp, °C	Time, h	$SOCl_2$, %	Convn,[c] %	Tar, %[d]
0.5	2.3	$SbCl_5$ (0.4)	25	21.5[e]	65	73	0.1
0.5	2.3	$SbCl_5$ (0.4)	65	1.0[e]		7	
0.5	2.3	$SbCl_5$ (0.4)	90	1.0[e]		12	
0.5	2.3	$SbCl_5$ (1.2)	90	4.0[e]	76	86	0.2
0.5	2.3	$SbCl_5$ (1.2)	120	3.0[e]	57	66	0.2
0.5	3.0	$SbCl_5$ (1.2)	120	3.0[e]	60	73	0.3
0.5	3.0	$SbCl_5$ (0.3)	100	3.0	91	100	0.5
0.2	7.5	$SbCl_5$ (2.0)	120	2.0	82	100	0.2
0.2	7.5	$FeCl_3$ (2.5)	140	2	81	100	3.1
0.2	7.5	$AlCl_3$ (3.8)	65	2	0	27	>11
0.2	7.5	$AlCl_3$ (3.8)	120	2	59	76	2.6
0.2	7.5	$AlCl_3$ (5.0)	110	10	83	100	3.8
0.2	7.5	$AlCl_3$ (5.0)	140	2	78	100	3.3
0.2	7.5	$SbCl_3$ (5.0)	150	6	17	47	
0.2	7.5	$AsCl_3$ (9.9)	150	10	15	46	
0.2	7.5	$TiCl_4$ (4.5)	150	10	31	80	
0.5	3.0	$TiCl_4$ (4.5)	100	18.5	Trace	Low	
0.2[f]	7.5	$SbCl_5$ (2.0)	90	2		97	0.2
0.2[f]	7.5	$SbCl_5$ (2.0)	120	2		92	0.2
0.2[f]	7.5	$FeCl_3$ (3.7)	90	2		100	1.3
0.2[f]	7.5	$FeCl_3$ (3.7)	120	2		100	1.5
0.2[f]	7.5	$AlCl_3$ (3.7)	90	2		35	1.6
0.2[f]	7.5	$AlCl_3$ (3.7)	120	2		40	2.4
0.2	5.0	TBP[g] (3.9)	130–160[h]	5	14	29	
0.2	7.5	TBP[g] (8.1)	140–155[h]	7	Low	42	

[a] In addition to the runs tabulated, $SnCl_4$, $ZnCl_2$, $MgCl_2$, BCl_3, $HgCl_2$, and $SiCl_4$ were tested at the 5–10 mol % level with 0.2 mol of HCMX and 1.5 mol of SO_2 for 10 h at 150 °C. Conversions did not exceed 30%, the value reached with no catalyst under these conditions. The products from $FeCl_3$ catalysis were deep red, and those from $AlCl_3$ were amber; neither could be decolorized by distillation. The products from $SbCl_5$ were orange, which color was readily removed by simple topping through a fractionating column. [b] Run by the general procedure in the Experimental Section. See Table I for explanation of column headings. [c] Fraction of total CCl_3 groups converted to COCl, as determined by GC analysis of distilled product. [d] Weight of undistillable pot residue/theoretical weight of product. [e] In all runs except these, the bomb was allowed to cool slowly in its heater and discharged the next day (after 12–18 h). In these[e] runs, the bomb was cooled as rapidly as possible after the expiration of the heating period. See Experimental Section. [f] Starting with hexachloro-*p*-xylene, the product is terephthaloyl chloride. [g] Di-*tert*-butyl peroxide. [h] The reaction mixture was held at the lower temperature for 3 h, then gradually heated to the upper temperature.

Typical conditions for preparing isophthaloyl chloride in high yield and conversion involve heating a mixture of 156 g (0.5 mol) of HCMX and 96 g (1.5 mol) of sulfur dioxide in a 240-ml shaker tube lined with Hastelloy C. The reaction is complete in 2–3 h at 230 °C. The yield of ICl is about 95%, of thionyl chloride 90%, and the small amount of tar is readily removed by distillation. Most of the losses are mechanical.

Catalysis. The chief drawbacks to the procedure outlined are the high temperature required, the resultant high pressure, and, above all, the extreme corrosiveness of hot thionyl chloride. Common autoclave metals are severely attacked. Even Hastelloy C is slowly corroded. (Platinum and tantalum were not tested.) Since corrosion-resistant high-pressure vessels are expensive, catalysts were sought to reduce the operating

Table III. Reaction of $XC_6H_4CCl_3$ with Sulfur Dioxide (Uncatalyzed)[a]

Registry no.	X	SO_2, mol ratio	Temp, °C	Time,[b] h	$SOCl_2$,[c] %	Convn,[d] %
98-07-7	H	3.3	185	2	50	65
488-98-2	*o*-F	3.3	185	2	42	53
401-77-4	*m*-F	3.3	185	2	61	64
402-42-6	*p*-F	3.3	185	2	81	91
2136-89-2	*o*-Cl	3.3	185	2	25	42
2136-81-4	*m*-Cl	3.3	185	2	14	25
5216-25-1	*p*-Cl	3.3	185	2	66	66
13014-18-1	2,4-Cl_2	3.3	185	2	26	43
13014-24-9	3,4-Cl_2	3.3	185	2	14	25
27428-84-8	*m*-ClCO	4.0	185	2	6	10
881-99-2	*m*-CCl_3[e]	5.0	185	2	78[f]	56[f]
	H	3.3	210	2.25	82	100
	o-Cl[e]	1.5	240	1	67	70
	m-Cl[e]	1.5	240	1	83	95
	p-Cl[e]	2.5	220	1	61	75
	2,4-Cl_2	3.3	210	2	78	100
	3,4-Cl_2	3.3	210	2	72	98
	m-ClCO	4.0	210	2	24	45
	m-CCl_3[e]	5.0	210	2	70[f]	72[f]

[a] Performed as described in the Experimental Section with 0.3 mol of $ArCCl_3$ in a 240-ml Hastelloy C shaker tube. [b] Time at temperature cited, excluding heating and cooling times. [c] Percent of 0.3 mol. [d] Calculated from GC analysis from the ratio of $ArCCl_3$ to ArCOCl. [e] 0.2 mol of substrate was used. [f] Calculated as if one CCl_3 group were an inert substituent; the overall conversion is half this figure.

temperature, and thus the pressure and corrosiveness. A free-radical mechanism seemed probable; hence standard free-radical initiators were tested. Di-*tert*-butyl peroxide was moderately effective in the temperature range 130–160 °C, giving conversions two to three times those obtained in identical runs without catalysts. Other initiators were tested in the temperature ranges at which they are customarily employed as radical polymerization initiators (70–110 °C). Benzoyl peroxide was detectably active, while pelargonyl peroxide, *tert*-butylperoxy 2-ethylhexanoate, and azobisisobutyronitrile were inactive.

Since sulfuric acid can hydrolyze trichloromethylarenes to acid chlorides and carboxylic acids via the dichlorobenzyl cation, it was tested with sulfur dioxide. It was only moderately effective. Fluorosulfonic acid gave only tar with HCMX–SO_2; see part 2.

Lewis acids were next considered, and antimony pentachloride was tested first, with gratifying success. Typically, with 1 mol % of antimony pentachloride, a run like that described above was complete in 2 h at 90 °C (instead of 230 °C). In another case, a thermal run gave 1% conversion in 36 h at 80 °C, but addition of 0.3% of antimony pentachloride gave 73% conversion in 21.5 h at 25 °C. The lower temperatures permit operating below the critical temperature of sulfur dioxide; its vapor pressure is 18 atm at 80 °C and 34 atm at 110 °C. Moreover, the solubility of sulfur dioxide in HCMX is much greater at lower temperatures, so that only 20–50% excess is required, thus minimizing the costs of recovery. The yield of ICl is higher because less tar is formed, and corrosion is a much less serious problem. Representative examples of antimony pentachloride catalyzed runs are presented in Table II.

Several other Lewis acids were also tested. Ferric chloride and aluminum chloride were quite active, but they formed considerably more tar than antimony pentachloride.[8] Other catalysts, listed in order of decreasing activity, were antimony trichloride, titanium tetrachloride (at 150 °C), stannic chloride, and arsenic trichloride. Several others were completely inert, namely zinc chloride, magnesium chloride (anhydrous), boron chloride, mercuric chloride, silicon tetrachloride, and titanium tetrachloride (at 100 °C). No obvious explanation is available for the peculiar fact that titanium tetrachloride gave 80% conversion in 10 h at 150 °C but negligible conversion in 18 h at 100 °C. Transition metal cluster compounds which can form large stable M_xCl_n anions might be useful.

Other Trichloromethylarenes. Various trichloromethylarenes were tested in both the thermal and catalyzed reactions. Hexachloro-*p*-xylene reacts as well as the meta isomer to give trichloro-*p*-toluyl chloride and terephthaloyl chloride (Tables I and II). Ring-chlorinated derivatives of HCMX likewise react, but usually more slowly than the parent; see part 4 of this series.

The relative reactivities of trichloromethylarenes are markedly influenced by other substituents on the ring, as deduced from relative conversions at the same temperature. Absolute rates were not determined because the available pressure equipment did not permit "instantaneous" heating of a loaded bomb to a high temperature, nor sampling during a run. Somewhat different substituent effects were noted when comparing catalyzed and uncatalyzed reactions.

The thermal reactions yielded little tar (high-boiling or undistillable material), so that conversion is a satisfactory measure of rate; see Table III. Electron-attracting groups retard the reaction. Thus for meta-substituted benzotrichlorides, the conversions decreased in the order $H \geq F > Cl \geq CCl_3 > COCl$; for ortho substituents, $H > F > Cl$; for para substituents, $F > H = Cl$. 2,4-Dichlorobenzotrichloride reacts more completely than the 3,4-dichloro isomer. A given substituent has different effects, depending on its orientation. For fluorine, the order is $p > m > o$; for chlorine, $p > o > m$ at 185 °C, but at 240 °C, $m > o$. The results are explicable in terms of the electron-attracting ability of the substituent, combined with the possibility of mesomeric electron release to the developing carbocation from fluorine (see Mechanism). A steric retardation is apparent in the differences between the ortho and para halogens.

The catalyzed ($SbCl_5$, $FeCl_3$, $AlCl_3$) reactions, on the other hand, yielded a great deal of tar when the ring was not strongly deactivated. The major tar-forming reaction is apparently Friedel–Crafts condensation of the first-formed acyl chloride with unchanged trichloromethylarene. In several experiments, the fraction boiling higher than acid chloride was inspected by infrared, and it showed both ketone carbonyl and trichloromethyl functions. No attempt was made to characterize it

Table IV. Reaction of $XC_6H_4CCl_3$ with Sulfur Dioxide (Catalyzed by $SbCl_5$)[a]

X	Temp, °C	$SOCl_2$, %[b]	Convn, %[c]	ArCOCl yield, %[d]
H	65	Trace	28[e]	4
o-F	65	Trace	8[e]	4
m-F	65	46	55	48
p-F	65	Low	20	Low
o-Cl	65	14	37[e]	32
m-Cl	65	50	76	68
p-Cl[f]	65		14	15
H	90	Trace	<50[e]	9
o-F	90	34	80[e]	38
m-F	90	80	95	82
p-F	90	71	70	60
o-Cl	90	65	95	81
m-Cl	90	49	70	67
p-Cl[f,g]	90	40	55	50
2,4-Cl_2	90	80	99	90
3,4-Cl_2	90	33	51	55
m-ClCO	90	77	98	96
o-F[h]	115	50	95[e]	50
m-F[h]	115	46	55[i]	41
p-F[h]	115	55	60[e,j]	41
m-ClCO[h]	115	82	99	90

[a] Conditions: 0.3 mol of $ArCCl_3$, 1.0 mol of SO_2, 1.3 mol % $SbCl_5$. Heated for 2 h at specified temperature. [b] Percent of 0.3 mol. [c] Unrecovered $ArCCl_3$ as calculated from weight and GC analysis of distilled product. [d] Calculated from weight and GC analysis of distilled product. [e] A great deal of tar and also volatile byproducts were formed. [f] 1.5 mol of SO_2. [g] 0.8 mol % of $SbCl_5$. [h] 1.2 mol of SO_2. [i] Less tar formed than at 90 °C. [j] More tar formed than at 90 °C.

further. In a test experiment, benzoyl chloride condensed readily with benzotrichloride in the presence of ferric chloride to yield the same sort of high boiler; benzoyl chloride did not self-condense. Curiously, less tar was usually formed when the catalyzed reaction was run at a higher temperature for a shorter time, indicating that the activation energy for Friedel–Crafts condensation is smaller than that for acid chloride formation. Antimony pentachloride is normally regarded as a weak Friedel–Crafts catalyst; hence it was surprising to find it acting as a condensing agent here. Evidently, in sulfur dioxide solution, antimony pentachloride is much more reactive as a Friedel–Crafts catalyst than it is in the usual hydrocarbon or halocarbon solvent.

Conclusions about relative reactivities in the catalyzed reaction are necessarily tentative because of the tar-forming side reactions. Not only do these reduce yields and mask conversions, but the tar may well complex strongly with the Lewis acid and deactivate it. With this reservation, the chlorobenzotrichlorides are more reactive at 65 °C than their fluoro analogues, in any position, and both seem to be more reactive than benzotrichloride itself. Either chlorine or fluorine is more activating in the meta than in the ortho or para position. However, at 90 °C, fluorine activates more than chlorine, and the *m*-chlorocarbonyl is still more effective. 2,4-Dichloro is more reactive than 3,4-dichloro, and the former is about as effective as *m*-ClCO. At 115 °C, for fluorine, the activities fall off in the order $o > p > m$; the ClCO group is still most activating. See Table IV.

Although theoretical conclusions are not on firm experimental ground because of the tar problem, it seems clear that quite different substituent effects occur in the catalyzed reaction, compared to the thermal. Very likely, the rate-controlling step is different.

To see whether these new reactions could convert aliphatic polychlorides to acid chlorides, aliphatic $RCCl_3$ compounds were examined cursorily. Carbon tetrachloride is known to react with sulfur dioxide at 160 °C in the presence of aluminum chloride to yield phosgene and thionyl chloride.[9] The thermal reaction had not been reported, and indeed, it did not occur at 280 °C. Likewise, "methylchloroform", CH_3CCl_3, was inert to sulfur dioxide at 250 °C for 7 h; with 1% of antimony pentachloride, no acetyl chloride was formed in 6 h at 130 °C, although a little vinylidene chloride appeared, and also tar. However, hexachloropropene yielded 36% of trichloroacrylyl chloride and some trichloroacrylic acid when it was heated with sulfur dioxide for 2 h at 250 °C; compare the results with metal oxides.[6] Evidently, reaction occurs readily only when the developing cation $RCCl_2^+$ is stabilized by a vinyl or aryl group.

Benzal chloride ($C_6H_5CHCl_2$) and other dichloromethylarenes also react with sulfur dioxide. The results are discussed in part 3 of this series. Such compounds are present in incompletely chlorinated xylenes.

Trifluoromethylarenes were studied briefly. Benzotrifluoride failed to react thermally with sulfur dioxide at temperatures to 270 °C. It also failed to react in 18 h at 150 °C in the presence of 2 mol % of antimony trifluoride. 2-Chlorobenzotrifluoride under the latter conditions yielded a little acid fluoride but mostly high-boiling liquid and solid products obviously derived from condensation reactions; less stringent conditions were not tested. Hexafluoro-*m*-xylene likewise failed to react thermally with sulfur dioxide at 270 °C. When it was held for 18 h at 150 °C with 4 mol of sulfur dioxide and 2.7 mol % of antimony pentafluoride, 86% of the CF_3 groups were converted to COF, and the product was a mixture of isophthaloyl fluoride and trifluoro-*m*-toluyl fluoride. Clearly the trifluoromethyl group is *much* less reactive than the trichloromethyl group under comparable conditions. Perfluoro-*n*-octyl iodide did not react with sulfur dioxide and antimony pentafluoride at 110 °C in 5 h; it was not tested at 200 °C, where it is known to dissociate to perfluoroalkyl radicals.

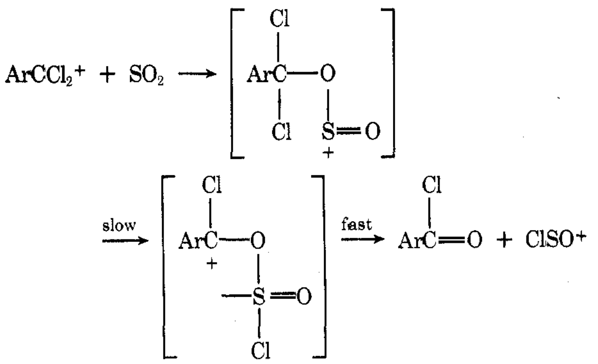
Mechanisms of the Sulfur Dioxide Reactions. The Lewis acid catalyzed reaction doubtless follows the straightforward ionization path:

$$ArCCl_3 + SbCl_5 \dashrightarrow ArCCl_2^+SbCl_6^- \qquad (10)$$

Ionization is favored by the solvent sulfur dioxide. Thus when a sulfur dioxide solution of *m*-chlorobenzotrichloride in a glass tube is treated with a little antimony pentachloride at −10 °C, a red solid precipitates which dissolves when the mixture is warmed to 50 °C. However, no permanent reaction takes place in 1 h at 55 °C or in 4 subsequent days at 25 °C; no detectable *m*-chlorobenzoyl chloride was formed. Apparently the cation formed readily but failed to react with sulfur dioxide under these mild conditions. Red to orange dichlorobenzyl cations have been observed when trichloromethylarenes are dissolved in oleum[2] and they are slowly converted to aroylium ions by the bisulfate ion present in equilibrium. Volz[10] has isolated and characterized phenyl- and mesityldichlorocarbonium hexachloroantimonates; carbon tetrachloride was his solvent. Although sulfur dioxide is an excellent solvent for carbocation study, its *reaction* with carbocations has not been previously noted.

The dichlorobenzyl cation is doubtless solvated by sulfur dioxide to form a structure like $ArCCl_2(OSO)_n^+$. To react further, a chlorine atom must be transferred to sulfur. This is probably the slow step in the reaction, for expulsion of the chlorothionyl cation with generation of the stable acid chloride would be easy.

Thionyl chloride may be formed by attack of the chlorothionyl cation on fresh trichloromethylarene or on hexachloroantimonate ion. The first of these probably occurs in



$$\mathrm{ArCCl_2^+} + \mathrm{SO_2} \longrightarrow \left[\mathrm{Ar}\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{-O-}\underset{+}{\mathrm{S}}\mathrm{=O}\right] \xrightarrow{\text{slow}} \left[\mathrm{Ar}\overset{\mathrm{Cl}}{\underset{+}{\mathrm{C}}}\mathrm{-O-}\underset{\mathrm{Cl}}{\mathrm{S}}\mathrm{=O}\right] \xrightarrow{\text{fast}} \mathrm{Ar}\overset{\mathrm{Cl}}{\mathrm{C}}\mathrm{=O} + \mathrm{ClSO^+} \quad (11)$$

the thermal reaction where hexachloroantimonate ion is absent. Other chlorine transfer equilibria may also be occurring.

$$\mathrm{ClSO^+} + \mathrm{ArCCl_3} \dashrightarrow \mathrm{ClSOCl} + \mathrm{ArCCl_2^+} \quad (12)$$

$$\mathrm{ClSO^+} + \mathrm{SbCl_6^-} \dashrightarrow \mathrm{ClSOCl} + \mathrm{SbCl_5} \quad (13)$$

$$\mathrm{ArCOCl} + \mathrm{SbCl_5} \dashrightarrow \mathrm{ArCO^+SbCl_6^-} \quad (14)$$

$$\mathrm{ArCO^+} + \mathrm{ArCCl_3} \dashrightarrow \mathrm{ArCOCl} + \mathrm{ArCCl_2^+} \quad (15)$$

The thermal reaction probably involves the same group of reactions, except that in the absence of the chlorophilic antimony pentachloride, ionization is much more difficult. Formation of the ion pair $\mathrm{ArCCl_2^+Cl^-}$ should require assistance by solvent sulfur dioxide, which is necessarily present in low concentration in the liquid phase above its critical temperature. The required high pressure is necessary to maintain even a small amount of dissolved sulfur dioxide. Very likely ionization is the slow step, since above 200 °C where the thermal reaction occurs, chlorine transfer in the solvated cation should be very rapid.

An alternative radical reaction probably occurs to a limited extent. As noted above, the rate of reaction at 130–160 °C is enhanced by a factor of 2–3 by addition of di-*tert*-butyl peroxide. A kinetic study should help in assessing the relative importance of ionization and radical mechanisms in the thermal reaction.

Experimental Section

Materials. Hexachloro-*p*-xylene was obtained from Aldrich Chemical Co. Hexachloro-*m*-xylene was prepared by photochlorination of *m*-xylene (1–2% *p*-xylene, 1% *o*-xylene) at 90 → 140 °C and purified by fractional vacuum distillation through a 1-m column packed with nickel Helipak (Podbelniak Co.) to remove pentachloro-*o*-xylene and hexachloro-*p*-xylene. The fluorobenzotrichlorides were prepared by photochlorination of the fluorotoluene, followed by fractional distillation. The chlorobenzotrichlorides and benzotrichloride itself were obtained from Hooker Chemical Co., and fractionated where necessary. Trichloro-*m*-toluyl chloride was prepared by photochlorination of *m*-toluyl chloride.[11]

Acid chlorides for reference were obtained from Aldrich. When necessary, they were converted to known amides or anilides for characterization.

All reactions with sulfur dioxide were conducted in a shaker tube of 240-ml capacity lined with Hastelloy C. The trichloromethylarene was added, and the tube was covered and purged with dry nitrogen while it was being chilled to −80 °C. The antimony chloride, where used, was added from a flame-dried pipet directly onto the frozen organic material; it was not allowed to run down the side of the tube, since colored impurities were made with this technique. The tube was then closed, pressure tested with nitrogen, and evacuated. Sulfur dioxide was then added through a coil of 0.125-in. copper tubing from a cylinder resting on a balance. In several experiments, the shaker tube was weighed before and after sulfur dioxide addition to verify the quantity added. The tube was then clamped in a heating shell behind a steel barricade and shaken horizontally at 180 strokes/min during the entire reaction. The temperature was monitored and controlled with a thermocouple in a well. The pressure was not usually read, because hot thionyl chloride rapidly destroys the Bourdon tubes in conventional pressure gauges; even a pressure-sensing cell, often used instead of a gauge, was damaged.

Heating to 100 °C required about 20 min, to 200 °C about 40 min, but the heating times were not very reproducible.[12] After the desired reaction time, the heater was shut off and the bomb was allowed to cool. In most of the thermal reactions, the bomb was left until the next morning before venting and discharging. Control experiments showed that no reaction occurred at room temperature without catalyst. With catalyzed reactions where the time was critical, the bomb was cooled with an air blast until cool enough to handle, then placed in a tub of cold water for a few minutes, then discharged quickly. Unfortunately, this procedure could never be standardized well enough to give reproducible conversion values for the more rapid reactions.

In some experiments on a larger scale, a 2-l. rocker bomb (Hastelloy C) was charged with the trichloromethylarene (and catalyst where used), chilled and evacuated, and heated to the desired temperature. Sulfur dioxide was added liquid phase through an automatic valve from a cylinder pressured with helium so as to maintain a constant internal pressure within the reactor. Nitrogen could not be used because it is too soluble in liquid sulfur dioxide.

The product was distilled, first at atmospheric pressure. Since it was saturated with sulfur dioxide, poor yields of thionyl chloride were obtained unless the exit tube from the apparatus was connected to a −10 °C trap to catch the thionyl chloride entrained with the gas. The acid chloride was then distilled at an appropriate reduced pressure.

The acid chloride was analyzed by gas chromatography, using a Varian Aerograph Model 202B instrument equipped with nickel filaments and a nickel block in its TC detector to minimize corrosion by the acid chloride. The 5 ft × 0.25 in. stainless steel columns were packed with 20% SE-30 on 60–80 mesh Chromosorb W AW-DMCS, and they were operated at an inlet pressure of 100 psig, helium flow 60 ml/min. The glass-lined injector port was maintained at 245 °C, the detector at 310 °C. For rapid scanning of mixtures, the initial temperature of the column was 170 °C, with linear programming at 4 °C/min. Better resolution for quantitative work was obtained with an initial temperature of 120 °C, isothermal for 3 min, then programmed at 6 °C/min. For these two different programs, the respective retention times for IPC were 4 and 10 min, for TCTC 6 and 15 min, for HCMX 8 and 18 min. Peak areas were measured by triangulation and corrected for detector response.

All the acid chlorides encountered in this work were known compounds. They were identified by their physical constants and spectral properties.[13]

Acknowledgment. I am indebted to Mr. Rayfield L. Taylor for skillful technical assistance. I would like to acknowledge numerous stimulating discussions with Drs. Thomas A. Johnson and Ian F. Dyson.

Registry No.—Sulfur dioxide, 7446 09-5.

References and Notes

(1) A general discussion of acid chloride preparation is given by H. Henecka in Houben-Weyl, "Methoden der Organischen Chemie", Vol. VIII, Georg Thieme Verlag, Stuttgart, 1952, p 463 ff. See also R. Stroh, *ibid.*, Vol. V/3, pp 862, 952. Detailed procedures can readily be located in *Organic Syntheses* with the aid of the Cumulative Indices to Collected Volumes I–V, pp 222–223.

(2) R. J. Gillespie and E. A. Robinson, *J. Am. Chem. Soc.*, **87**, 2428 (1965); N. C. Deno, N. Friedman, and J. Mockus, *ibid.*, **86**, 5676 (1964). A few of the numerous patents on this subject are U.S. Patents 1 793 917, 2 016 784, 3 835 187; German Patents 331 696, 708 149; French Patents 820 696, 820 697.

(3) U.S. Patent 3 835 187.

(4) German Patents 1 151 792, 1 166 764, 1 193 636; French Patent 820 698.

(5) R. C. Schreyer, *J. Am. Chem. Soc.*, **80**, 3484 (1958); U.S. Patent 2 856 425.

(6) W. W. Porterfield and S. Y. Tyree, *Inorg. Synth.*, **9**, 133 (1967); **4**, 104 (1953); **5**, 153 (1957); **7**, 163 (1963); and references cited therein.

(7) *Since clarity of presentation in these papers would not be enhanced by* constant repetition of six α's, the compound will be named HCMX and treated as a parent compound for naming of the ring chlorination products. These abbreviated names are felt to be much clearer than the more conventional Roman or Arabic numeral designations. Trichloro-*m*-toluyl chloride and isophthaloyl chloride will be abbreviated TCTC and IPC, respectively.

(8) In U.S. Patent 3 411 886, issued after this work was essentially complete, Burk and Turnquest disclosed the use of ferric chloride as catalyst for the *reaction of hexachloro-p-xylene with sulfur dioxide at room temperature.* Aluminum, zinc, titanium, cadmium, and manganese halides are stated to

be ineffective. This report contrasts sharply with our experience, in which aluminum and titanium chlorides are quite active *above room temperature*.

(9) U.S. Patent 2 393 247.

(10) H. Volz and M. J. Volz de Lecea, *Tetrahedron Lett.*, 3413 (1965); 5249 (1966).

(11) W. Davies and W. H. Perkin, Jr., *J. Chem. Soc.*, **121**, 2202 (1922).

(12) Different operators performed the bomb runs, and the heaters were controlled manually. The time to reach 200 °C might vary ±10 min. Cooling from 250 °C to 100 °C usually required about 30 min.

(13) Much of the subject matter of these four papers has been disclosed in the following U.S. Patents (C. S. Rondestvedt, Jr., patentee): 3 668 247 (1972); 3 681 451 (1972); 3 681 452 (1972); 3 681 453 (1972); 3 681 454 (1972); 3 775 476 (1973); 3 806 545 (1974).

New Syntheses of Aromatic Acid Chlorides from Trichloromethylarenes. 2. Reaction with Sulfur Trioxide, Phosphorus Pentoxide, and Other Nonmetal Oxides

Christian S. Rondestvedt, Jr.

Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware 19898

Received April 27, 1976

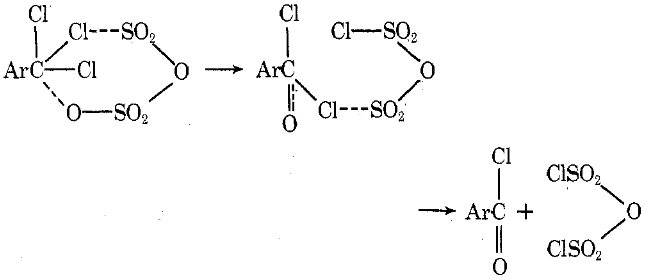
Trichloromethylarenes (benzotrichlorides) react with sulfur trioxide at 25–50 °C to yield aroyl chlorides and pyrosulfuryl chloride. Yields of both products are high when the arene also bears electron-withdrawing substituents, but benzotrichloride itself undergoes extensive sulfonation even at −10 °C. The reaction is interpreted in terms of attack of dimeric sulfur trioxide on chlorine, since, even with a deficiency of sulfur trioxide, sulfuryl chloride is never seen. Pyrosulfuryl chloride was prepared in 90% yield from sulfur trioxide and carbon tetrachloride, a marked improvement over the *Inorganic Syntheses* yield. Trichloromethylarenes also react with phosphorus pentoxide at 190–275 °C to yield aroyl chloride and phosphorus oxychloride, mostly in high yields. Electron-attracting substituents retard the reaction unless they also raise the boiling point to permit higher reaction temperatures. Various phosphoric acids and phosphate salts also react. Sodium chlorate, potassium nitrate, and selenium dioxide also react thermally with trichloromethylarenes to yield acid chlorides and inorganic products, but the reactions were too dangerous for detailed study.

Conversion of trichloromethylarenes to aroyl chlorides by heating with sulfur dioxide alone, or with Lewis acid catalysis, requires a pressure vessel.[1] Reagents which would be effective at atmospheric pressure were sought and found.

Sulfur Trioxide. Sulfur trioxide reacted rapidly at 25–50 °C with hexachloro-*m*-xylene (HCMX)[2] to form isophthaloyl chloride (IPC). However, the inorganic product was not sulfuryl chloride (SO_2Cl_2) but rather pyrosulfuryl chloride ($ClSO_2OSO_2Cl$). Four moles of sulfur trioxide was required to obtain a quantitative yield of IPC.

$$m\text{-}C_6H_4(CCl_3)_2 + 4SO_3 \rightarrow m\text{-}C_6H_4(COCl)_2 + 2Cl_2O_5S_2 \qquad (1)$$

The reaction does not proceed via sulfuryl chloride, since pyrosulfuryl chloride is not formed from sulfuryl chloride and sulfur trioxide.[3] Very likely the reaction involves dimeric sulfur trioxide attacking a chlorine atom, perhaps through a cyclic intermediate.



No significant sulfonation occurred with strongly deactivated rings, such as in HCMX and its para isomer. Similarly, halogen-substituted benzotrichlorides gave high yields of the halobenzotrichloride and pyrosulfuryl chloride, as shown in Table I. With *p*-chloro- and *p*-fluorobenzotrichlorides a small amount of high-boiling material was noted; this may be sulfone or sulfonyl chloride.

Benzotrichloride itself reacted very rapidly with 2 mol of sulfur trioxide. Even with a deficiency of sulfur trioxide or in ethylene dichloride solvent at −10 °C, the blood-red solution formed a great deal of tarry, high-boiling product, as well as benzoyl chloride. Gelfand[4] prepared *m*-chlorosulfonylbenzoyl chloride in 65% yield by heating benzotrichloride with 2 mol of sulfur trioxide at 140 °C. Under his conditions, sulfonation is much more rapid than the tar-forming side reactions.

The present reaction is reminiscent of the standard preparation of pyrosulfuryl chloride, in which sulfur trioxide reacts with carbon tetrachloride.[5] The reported yield is 45–50%. We repeated this procedure and obtained pyrosulfuryl chloride in over 90% yield. Sveda used sulfur trioxide obtained by distilling oleum, but since we used pure Sulfan B, we suggest that our greatly improved yield results from the absence of protons in Sulfan B.

Phosphorus Oxides. Phosphorus pentoxide reacts smoothly with trichloromethylarenes above about 190 °C at atmospheric pressure to form aroyl chloride and phosphorus oxychloride, as illustrated with hexachloro-*m*-xylene (HCMX).

$$3C_6H_4(CCl_3)_2 + 2P_2O_5 \rightarrow 3C_6H_4(COCl)_2 + 4POCl_3 \qquad (2)$$

The reaction is simply performed by heating a stirred mixture of the trichloromethylarene with a small excess of phosphorus pentoxide under a simple fractionating column. When the phosphorus oxychloride has been removed, the product is distilled in vacuo. High yields of both products are readily obtained.

This reaction is somewhat surprising, because the high affinity of phosphorus for oxygen suggests that carbon would readily yield an oxygen atom to phosphorus. Thus aldehydes and ketones are converted to dichloromethylarenes by phosphorus pentachloride, although acid chlorides are *not* converted to trichloromethylarenes by this reagent.