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

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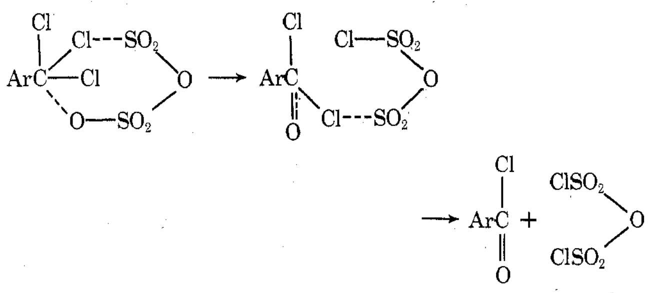
Trichloromethylarenes (benzotrichlorides) react with sulfur trioxide at 25–50 °C to yield aroyl chlorides and pyrosulfuryl chloride. Yields of both products are high when the arene also bears electron-withdrawing substituents, but benzotrichloride itself undergoes extensive sulfonation even at −10 °C. 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.

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

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).

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

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.

Table I. Trichloromethylarenes and Sulfur Trioxide[a]

Registry no.	$ArCCl_3$	Time, h	Temp, °C	ArCOCl Yield, %	ArCOCl Bp, °C (mm)	ArCOCl Registry no.	$Cl_2O_5S_2$ yield, %
402-42-6	$p\text{-}FC_6H_4CCl_3$	0.5	−5				
		2.0	20–40	85	104 (41)	403-43-0	64
5216-25-1	$p\text{-}ClC_6H_4CCl_3$	0.5	−10				
		2.0	25	81	128–132 (44)	122-01-0	71
13014-24-9	$3,4\text{-}Cl_2C_6H_3CCl_3$	0.7	10				
		3.5	10–56	85	121–123 (14)	3024-72-4	98
881-99-2	$m\text{-}C_6H_4(CCl_3)_2$	0.1	50				
		1.5	45–50	87[b]	125–127 (5)	99-63-8	86
68-36-0	$p\text{-}C_6H_4(CCl_3)_2$	0.75	20–30				
		3.6	20–75	96[c]	mp 80–81	100-20-9	95

[a] Sulfur trioxide (2+ mol/mol CCl_3) was added dropwise at the first temperature over the time given. The temperature was then gradually raised in the range given over the second time span. [b] Isophthaloyl chloride. [c] The terephthaloyl chloride was somewhat discolored; less color would probably be obtained at a lower temperature.

Table II. Trichloromethylarenes and Phosphorus Pentoxide[a]

Registry no.	$ArCCl_3$	P compd	ArCOCl, %	$POCl_3$, %	ArCOCl registry no.
98-07-7	$C_6H_5CCl_3$	P_2O_5	88	80	98-88-4
401-77-4	$m\text{-}FC_6H_4CCl_3$	P_2O_5	16	23[b]	1711-07-5
2136-89-2	$o\text{-}ClC_6H_4CCl_3$	P_2O_5	84	90	609-65-4
13014-18-1	$2,4\text{-}Cl_2C_6H_3CCl_3$	P_2O_5	89[c]	85	89-75-8
	$m\text{-}C_6H_4(CCl_3)_2$	P_2O_5	92[d]	93	
	$p\text{-}C_6H_4(CCl_3)_2$	P_2O_5	84	98	
	$m\text{-}C_6H_4(CCl_3)_2$	HPO_3	28[e]		
	$m\text{-}C_6H_4(CCl_3)_2$	$H_3PO_4\text{–}SbCl_5$	49[e]	36	
	$m\text{-}C_6H_4(CCl_3)_2$	$Ca_3(PO_4)_2$	43[e]	36[f]	

[a] All were conducted with 5% excess of P_2O_5 over the theoretical one-third mol per CCl_3 group. See Experimental Section. [b] Conversion figure was obtained only after 11 h at 214 °C; a great deal of tar was formed. [c] About 10% of the $ArCCl_3$ was also present. [d] About 3% of the $ArCCl_3$ was also present. [e] Percentage of total CCl_3 groups converted. [f] Reaction was stopped before completion because of apparent decomposition.

Benzotrichloride itself reacted smoothly at the normal boiling point (190 °C) of benzoyl chloride. Electron-withdrawing ring substituents retarded the reaction markedly, but when they also raised the boiling point, the higher temperature compensated for this retardation. High yields were obtained with the chlorobenzotrichlorides. However, fluorine has little influence on the boiling point. The reaction with *m*-fluorobenzotrichloride was quite slow at 215 °C, and side reactions (anhydride formation?) became prominent. Use of a pressure still, with provision for continuous removal of phosphorus oxychloride, should permit rapid reaction and satisfactory yields with the fluorobenzotrichlorides. The results are collected in Table II.

Electron-donating ring substituents should accelerate the reaction relative to benzotrichloride, but these benzotrichlorides are not readily available. One attempt to prepare *p*-methylbenzotrichloride by heating *p*-toluyl chloride with phosphorus pentachloride at 140 °C caused methyl group chlorination; the product was a mixture of α-chloro- and α,α-dichlorotoluyl chloride.

Carbon tetrachloride reacted readily with sulfur trioxide to form pyrosulfuryl chloride and phosgene, as discussed above.[6] However, it did not react significantly with phosphorus pentoxide at 250–270 °C in a pressure vessel; only traces of phosgene and phosphorus oxychloride were detected.

Phosphorus pentoxide is inconvenient to handle and store. We therefore examined other oxyphosphorus(V) compounds. Tricalcium phosphate reacted with HCMX at a moderate rate at 290 °C. After 1 h, during which 36% of the theoretical phosphorus oxychloride was obtained, the distilling material suddenly became dark, as if pyrolysis were occurring. The distillable organic product was a mixture of isophthaloyl chloride (30%), trichloro-*m*-toluyl chloride (26%), and hexachloro-*m*-xylene (9%). Evidently phosphate ion is too basic.

Various phosphoric acids may be regarded formally as hydrated phosphorus oxides. Metaphosphoric acid (HPO_3) is $P_2O_5 \cdot H_2O$, orthophosphoric acid (H_3PO_4) is $P_2O_5 \cdot 3H_2O$, and syrupy 85% phosphoric acid is approximately $P_2O_5 \cdot 5H_2O$. The water portion should react stoichiometrically as

$$ArCCl_3 + H_2O \rightarrow ArCOCl + 2HCl \qquad (3)$$

and the dehydrated P_2O_5 should form $POCl_3$ according to eq 2. Commercial solid metaphosphoric acid in contact with 1 mol of HCMX melted at about 120 °C to form an insoluble lower layer which gradually solidified as the temperature was raised over 3 h to 290 °C. By this time the inorganic material had formed a glassy solid on the walls of the container above the liquid. Conversion of trichloromethyl groups was 10.7%. After 6 h at 295 °C, the conversion was 24.4%, and after 7 more h, 28.5%. This limiting conversion corresponds to the "water" content of metaphosphoric acid, and the phosphorus oxide must have been converted to a highly condensed polyphosphoric acid. The solid required 2 days to dissolve in water, unlike the familiar phosphorus pentoxide.

When syrupy phosphoric acid was heated with HCMX, some liquid water distilled out and considerable tar was formed. However, when the acid was added to HCMX containing antimony pentachloride at 140–150 °C, the water portion reacted rapidly to form a white solid. When the mixture was heated further, the solid dissolved at about 210 °C. During 3 h at 280 °C, 36% of the theoretical phosphorus oxychloride was collected, and 49% of the trichloromethyl groups were converted. However, antimony pentachloride does not promote the reaction of ordinary phosphorus pentoxide with HCMX; hence in this case it functions as a catalyst for the water hydrolysis of HCMX. Zinc chloride did not accelerate the reaction. With aluminum chloride, a great deal of tar was formed at 190 °C.

Other Oxides. Other nonmetal oxides should be capable of reacting similarly with trichloromethylarenes. Silicon dioxide in several forms and particle sizes did not react at all with HCMX; neither did tetraethyl orthosilicate. Selenium dioxide reacted vigorously with 1 mol of HCMX when the temperature reached 170 °C; elementary selenium precipitated, and a white smoke filled the apparatus; its removal was rather difficult. This reaction was repeated with similar results. A solvent like trichlorobenzene might permit control of this reaction.

The chlorine oxides were attractive because their reaction would yield elementary chlorine which could be used again in the xylene chlorination. However, they are not easy to prepare and are too dangerous to consider for commercial use. Iodine pentoxide is not explosive, and the putative coproduct iodine pentachloride would dissociate to iodine and chlorine at high temperature (eq 4). Although it did react, a side reaction destroyed the product.

$$5ArCCl_3 + I_2O_5 \rightarrow 5ArCOCl + I_2 + 5Cl_2 \qquad (4)$$

Salts of Oxy Acids. The trichloromethyl group might react safely with nonmetal oxides as their salts. Sodium chlorate was selected initially because the inorganic coproduct would be useful chlorine, according to the following overall equation (three steps):

$$3ArCCl_3 + NaClO_3 \rightarrow 3ArCOCl + NaCl + 3Cl_2 \qquad (5)$$

When HCMX was heated with sodium chlorate, chlorine was evolved and IPC and TCTC were found in the mixture. Continued heating led to an eruption.

Potassium nitrate could react according to eq 6:

$$ArCCl_3 + KNO_3 \rightarrow ArCOCl + NO_2Cl + KCl \qquad (6)$$

When HCMX was heated with potassium nitrate, dinitrogen tetroxide and chlorine slowly were liberated above 200 °C. Acid chlorides were formed, but continued heating led again to an eruption.

Miscellaneous Oxygen Sources. Dimethyl sulfoxide reacted with HCMX at about 180 °C, giving some acid chloride, a volatile, evil-smelling mixture, and a great deal of tar.

$$ArCCl_3 + (CH_3)_2S{=}O \rightarrow ArCCl_2OS^+(CH_3)_2Cl^- \rightarrow ArCOCl + \text{other products}$$

Dimethylformamide reacted with benzotrichloride near 200 °C. The gas evolved was a mixture of dimethylamine and methyl chloride, perhaps containing hydrogen cyanide. Some *N,N*-dimethylbenzamide was isolated by distillation of the tarry product.

Sulfur (S_8) did not react with benzotrichloride in 2 h at 210–225 °C; neither sulfur monochloride nor thiobenzoyl chloride was detectable. The higher temperature obtainable with HCMX might open the S_8 ring to a reactive species.

Carbon disulfide did not react with benzotrichloride in 5 h at 220 °C; neither thiobenzoyl chloride nor thiophosgene could be detected. **Carbonyl sulfide** (carbon oxysulfide) did not react significantly with HCMX in 7 h at 250 °C; some high-boiling products were formed, but none of the possible inorganic products was detected.

Fluorosulfuric acid was expected to react like sulfuric acid, which will convert trichloromethylarenes to aroyl chlorides or aroic acids (depending on reaction conditions).[7] However, a complex mixture of products was obtained, including fluorosulfuric anhydride; sulfuryl chlorofluoride was not seen.

Experimental Section

Materials. The trichloromethylarenes were obtained as previously described.[1] Sulfur trioxide was purchased as Sulfan B (the stabilized γ form) from Allied Chemical Co., General Division. Phosphorus pentoxide was occasionally used as the ordinary powdered form, but in most experiments, Granusic granular phosphorus pentoxide was obtained from J. T. Baker Co. This form of the reagent could be handled conveniently without a drybox.

Sulfur Trioxide. Molten HCMX (1 mol) was stirred at 50 °C while sulfur trioxide (4.1 mol) (*Caution:* highly corrosive) was added from a dropping funnel over 5–10 min. The mixture was then stirred for 1.5 h near 50 °C, then distilled. Pyrosulfuryl chloride was collected near 69 °C (40 mm) and isophthaloyl chloride at 125 °C (5 mm), mp 40–41 °C. Hexachloro-*p*-xylene (mp 110 °C) was used as a coarse powder, and the sulfur trioxide was added at room temperature before the mixture was heated to 75 °C. The halobenzotrichlorides were held just above their freezing points during the sulfur trioxide addition; the temperature was then gradually raised to 40–50 °C. Details and yields are given in Table I.

Pyrosulfuryl chloride was also prepared from sulfur trioxide and carbon tetrachloride by a slight modification of the Sveda procedure.[5] The two reagents were mixed at room temperature; no heat was evolved. When the mixture was cautiously heated, a vigorous reaction set in at about 55 °C, and phosgene was liberated so rapidly that the stoppers blew out of the flask. Use of wide-bore connecting tubes would prevent this problem. Despite the accident, pure pyrosulfuryl chloride was isolated in 90% yield. Needless to say, the highly toxic phosgene must be handled in an efficient hood, and the effluent gas must be passed through an effective caustic scrubber followed by an ammonium hydroxide scrubber.

Phosphorus Pentoxide. Equivalent (eq 3) quantities of the reactants, or up to 5% excess of phosphorus pentoxide, were mixed in a flame-dried flask equipped with a motor stirrer (Trubore bearing, glass paddle), thermometer, and a fractionating column capable of separating phosphorus oxychloride (bp 108 °C) from the organic acid chloride. A larger excess of phosphorus pentoxide greatly increased the quantity of undistillable tar (anhydride?), and a deficiency merely decreased conversion. The mixture was heated to the boil and phosphorus oxychloride was removed as it formed. When the reaction was complete, in 2–3 h for HCMX or its para isomer, in 4–6 h for the monotrichloromethylarenes, the flask was arranged for vacuum distillation and the product was taken over rapidly to separate it from tar. The acid chloride was assayed by GC[1] and purified as required by fractional distillation or crystallization. It was characterized by its infrared spectrum and physical properties. The results are presented in Table II.

Curiously, addition of phosphorus pentoxide *in portions* during the reaction led to much lower yields of acid chloride. Apparently some intermediate phosphorus compound is formed after breaking the P_4O_{10} tetrahedron. After the mixture contains acid chloride, *fresh* P_4O_{10} reacts with it to form high-boiling by-products.

Nonmetal Oxides. HCMX was heated with 0.2 mol (eq 4) of iodine pentoxide. At about 160 °C, chlorine began to escape (greenish-yellow liquid at −80 °C, bp −34 °C). Then an orange solid (ICl_3?) appeared in the stillhead, and at 190 °C a brown liquid (ICl?) began to reflux vigorously. The ensuing exothermic reaction could not be controlled. The pot contents foamed vigorously and soon became an intractable polymeric solid. Crystalline iodine sublimed into the stillhead and receiver, and more chlorine collected in the trap. No IPC could be distilled out at 0.1 mm.

Salts of Oxy Acids. When HCMX was heated with 0.67 mol of sodium chlorate, the solid dissolved at 70 °C. Solid then precipitated at 178 °C (NaCl?) as chlorine evolution began. At 206 °C the reaction became exothermic, but it was controlled by lowering the heating bath. After 1 h at 200–230 °C, GC analysis showed the presence of considerable IPC and TCTC, over half of the original HCMX, and assorted ring-chlorination products. The mixture was cooled to about 150 °C and a further 0.67 mol of $NaClO_3$ was added. Chlorine was liberated as soon as the solid struck the liquid. On further heating to 173 °C, the mixture erupted from the flask. Other experiments with different heating regimens led eventually to the same results. The reaction, though exciting, was deemed unattractive for further study.

When equimolar amounts of HCMX and potassium nitrate were heated together, a dark-brown liquid began to distill at about 200 °C. Its boiling point behavior suggests that it was a mixture of chlorine and dinitrogen tetroxide. Slow distillation continued while the mixture was held for 1 h at 265–288 °C. Then it too erupted.

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 trioxide, 7446-11-9; phosphorus pentoxide, 1314-56-3; tricalcium phosphate, 7758-87-4; metaphosphoric acid, 10343-62-1; phosphoric acid, 7664-38-2; selenium dioxide, 7446-08-4; iodine pentoxide, 12029-98-0; sodium chlorate, 7775-09-9; potassium nitrate, 7757-79-1; dimethyl sulfoxide, 67-71-0; dimethylformamide, 68-12-2.

References and Notes

(1) C. S. Rondestvedt, Jr., *J. Org. Chem.*, preceding paper in this issue.

(2) See footnote 7, ref 1, for a discussion of the nomenclature used in these papers, and footnote 13 for a list of patent disclosures.

(3) E. Hayek and K. Hinterauer, *Monatsh. Chem.*, **82,** 205)1951); V. Grignard and P. Muret, *C. R. Acad. Sci.*, **183,** 581, 713 (1926).

(4) S. Gelfand, U.S. Patent 3 322 822 (1967).

(5) M. Sveda, *Inorg. Synth.*, **3,** 124 (1950).

(6) A. T. Hallowell and G. T. Vaala, U.S. Patent 2 393 247, showed that carbon tetrachloride will also react with sulfur dioxide if catalyzed by aluminum chloride to yield thionyl chloride and phosgene.

(7) For example, see R. J. Gillespie and E. A. Robinson, *J. Am. Chem. Soc.*, **87,** 2428 (1965).

New Syntheses of Aromatic Acid Chlorides from Trichloromethylarenes. 3. Oxidative Chlorination of Methylarenes with Thionyl Chloride and Sulfur Dioxide

Christian S. Rondestvedt, Jr.

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

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Toluene, benzyl chloride, benzal chloride, and their ring-substitution products react with thionyl chloride above 200 °C to yield (substituted) benzoyl chlorides and sulfur monochloride. Added sulfur dioxide retards the reaction but gives cleaner products. Addition of molecular oxygen frequently improves the yields and conversions.

Previous papers in this series[1,2] described conversion of trichloromethylarenes to aroyl chlorides by heating them with sulfur dioxide, sulfur trioxide, or phosphorus pentoxide. The trichloromethylarenes are prepared by free-radical chlorination of methylarenes. With toluene or halotoluenes, this process is simple enough. However, substituents ortho to the methyl group greatly retard the introduction of a third chlorine on that methyl group. In some cases, e.g., 2,6-dichlorotoluene, chlorination stops at 2,6-dichlorobenzal chloride, and attempts to force it further cause chlorinolysis to 1,2,3-trichlorobenzene. *o*-Xylene is readily converted to the pentachloro derivative, but attempts to introduce the sixth chlorine are futile. Even with the unhindered *m*- and *p*-xylene, complete introduction of the sixth chlorine requires almost as much time as the preceding five; in large-scale manufacture, time is costly. Synthesis of isophthaloyl and terephthaloyl chlorides by any of the processes disclosed in the previous papers[1,2] must contend with incompletely chlorinated material.

$\alpha,\alpha,\alpha,\alpha',\alpha'$-Pentachloro-*m*-xylene (PCMX)[3] reacts with sulfur dioxide, sulfur trioxide, or phosphorus pentoxide to yield initially α,α-dichloro-*m*-toluyl chloride (DCTC);[3] the dichloromethyl group does not react readily under conditions which convert the trichloromethyl group completely to carbonyl chloride. Though DCTC can be separated from isophthaloyl chloride by fractionation, the process is expensive when pure isophthaloyl chloride is required.

A solution to the problem was indicated by the observation that prolonged heating of underchlorinated *m*-xylene with excess sulfur dioxide converted DCTC to IPC. Thionyl chloride performed oxychlorination of the C–H bond, and sulfur dioxide converted the trichloromethyl group to carbonyl chloride. Suggested partial reactions are

$$\mathrm{Cl_3CC_6H_4CHCl_2 + SO_2 \rightarrow ClCOC_6H_4CHCl_2 + SOCl_2} \quad (1)$$

$$\mathrm{3ClCOC_6H_4CHCl_2 + 4SOCl_2 \rightarrow 3ClCOC_6H_4CCl_3 \;.\; s_2Cl_2 + 2SO_2 + 3HCl} \quad (2)$$

$$\mathrm{ClCOC_6H_4CCl_3 + SO_2 \rightarrow C_6H_4(COCl)_2 + SOCl_2} \quad (3)$$

In sum:

$$\mathrm{3Cl_3CC_6H_4CHCl_2 + 4SO_2 \rightarrow 3C_6H_4(COCl)_2 + 3\,HCl + S_2Cl_2 + 2SOCl_2} \quad (4)$$

Since step 2 is slow relative to conversion of trichloromethyl to carbonyl chloride (1 and 3), the reaction was studied in some detail in an effort to accelerate it.

Benzal chloride and sulfur dioxide do not yield benzaldehyde and thionyl chloride, but rather benzoyl chloride and inorganic products in low yield. A much better yield of benzoyl chloride was obtained by heating benzal chloride with thionyl chloride at 220 °C. Benzaldehyde, benzyl chloride, and even toluene were similarly converted to benzoyl chloride. A variety of substituted toluenes yielded substituted benzoyl chlorides, frequently in high yield, and especially when sulfur dioxide was used together with thionyl chloride (see below). The process goes by stepwise replacement of hydrogen, because incomplete reactions with toluenes yielded (substituted) benzyl chloride, benzal chloride, and benzotrichloride.

$$\mathrm{ArCH_3 + 3SOCl_2 \rightarrow ArCOCl + SO_2 + S_2Cl_2 + 3HCl} \quad (5)$$

Pollak and Rudich[4] noted the ability of thionyl chloride to chlorinate the side chain of various methylarenes. Under drastic conditions (250–320 °C) acid chlorides were sometimes detected; disulfur dichloride (sulfur monochloride) was not reported, though they occasionally encountered free sulfur.

In our work, performed mostly in a pressure bomb lined with Hastelloy C, a high-nickel alloy, ring chlorination of toluene and especially the xylenes was a nuisance which lowered the yield of the desired acid chloride. In a glass-lined