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.

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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

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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

Table I. Oxychlorination with Thionyl Chloride [a]

Registry no.	Substrate, S	Mol of S	Mol of SO_2/ mol of S	Mol of $SOCl_2$/ mol of S	Temp, °C	Time, h	ArCOCl, % yield	Purity, %	Registry no.
100-52-7	C_6H_5CHO	0.3		1.2	240	4	68	98	98-88-4
98-87-3	$C_6H_5CHCl_2$	0.3		1.0	240	6	95	70[b]	
100-44-7	$C_6H_5CH_2Cl$	0.4		2.0	220	2	57	80	
108-88-3	$C_6H_5CH_3$	0.4		3.0	220	2	84	80[c]	
	$C_6H_5CH_3$	0.4	1.25	2.25	220	2	50	c	
	$C_6H_5CH_3$[d]	0.4	1.25	3.0	220	2, 1	89	98	
95-52-3	o-$FC_6H_4CH_3$	0.3		3.0	235	3.5	89	70[c]	393-52-2
352-70-5	m-$FC_6H_4CH_3$	0.4	1.1	3.5	235	3.5	70	95[c]	1711-07-5
352-32-9	p-$FC_6H_4CH_3$	0.3		3.0	230	3	70	75[c]	403-43-0
	p-$FC_6H_4CH_3$	0.3	1.67	3.0	200	3	Low		
95-49-8	o-$ClC_6H_4CH_3$	0.5		3.0	240	4	76	90[c,e]	609-65-4
95-73-8	2,4-$Cl_2C_6H_3CH_3$	0.4	1.3	4.0	230–245	5.3	95	90[c,f,g]	89-75-8
118-69-4	2,6-$Cl_2C_6H_3CH_3$	0.3	1.0	3.3	255	6		h	
81-19-6	2,6-$Cl_2C_6H_3CHCl_2$	0.3	1.67	1.0[i]	230	8	34	90	4659-45-4
591-17-3	m-$BrC_6H_4CH_3$	0.25	3.0	1.0	235	3	67	95[j]	1711-09-7
106-38-7	p-$BrC_6H_4CH_3$	0.2		3.0	230	5	72	96[k]	586-75-4
98-59-9	p-$ClSO_2C_6H_4CH_3$	0.2		3.5	210	2		l	
99-04-7	m-$HOOCC_6H_4C$-$_3$ H_3	0.3	1.0	4.3	220	2		c	
1711-06-4	m-$ClCOC_6H_4CH_3$	0.4		3.0	210–235[m]	5	92	75[c]	99-63-8
	m-$ClCOC_6H_4CH_3$	0.4	0.75	3.67	210–235[m]	5	97	86[c]	
36747-51-0	m-$ClCOC_6H_4CH$-Cl_2	0.3	3.0	1.0[i]	240	4	92	95	
108-38-3	m-$C_6H_4(CH_3)_2$	0.3	0.5–2.0	6.0	200–240	2–6	n		

[a] The reactions were conducted in a 240-ml shaker tube lined with Hastelloy C, except as noted. See Experimental Section. [b] Some unchanged substrate was present. [c] $ArCHCl_2$ and $ArCH_2Cl$ were also present. [d] Run in glass. See detailed procedure in the Experimental Section. [e] Vented several times to keep pressure below 5000 psi. [f] Some 1,2,4-trichlorobenzene was formed by chlorinolysis. [g] A duplicate run with 0.25 mol of O_2 per mole of S gave mostly tar. [h] Low conversion. [i] Oxygen (0.25 mol per mole of S) was also added. The undistillable residue may contain binuclear compounds like chlorostilbenequinone. [j] m-Chlorobenzoyl chloride. [k] p-Chlorobenzoyl chloride. [l] ArCOCl was not formed under these conditions. Half of the TosCl was recovered, and also p-$ClC_6H_4CH_{3-n}Cl_n$. [m] The temperature was raised gradually during 5 h. [n] In numerous attempts, ring chlorination competed extensively with side-chain chlorination. About 50% of isophthaloyl chloride was obtained in the best runs.

bomb, ring chlorination was greatly reduced, but conversion of trichloromethyl compound to acid chloride was also reduced. When a toluene–thionyl chloride mixture in glass was heated with added nickel powder, Hastelloy C filings, or nickel chloride,[5] conversion to acid chloride was increased; unfortunately, ring chlorination of the toluene also increased. Ring chlorination was not a serious problem with toluenes carrying a ring-deactivating group such as halogen, trichloromethyl, or carbonyl chloride, even in the metal bomb.

Some unusual features in Table I deserve comment. Hot thionyl chloride caused chlorodesulfonation of p-toluenesulfonyl chloride; partly converted material had no side-chain chlorines. Pollak and Rudich[4] studied the thionyl chloride–tosyl chloride reaction but did not report the apparent inhibiting power of the chlorosulfonyl group on side-chain chlorination. *m(p)-Bromo*toluene gave *m(p)-chloro*benzoyl chloride. Replacement of bromine by chlorine may proceed through an unstable $ArBrCl_2$, analogous to chlorodeiodination via $RICl_2$.[6] m-Nitro- and p-cyanotoluene (not tabulated) gave only undistillable products above 180–200 °C, and no reaction at lower temperatures.

Sulfur dioxide itself is sometimes used as an oxidizing agent for methylarenes, usually with metal oxide catalysts. Toluene and m-xylene were not attacked by sulfur dioxide alone in a bomb at 200–250 °C. When sulfur dioxide was added initially to thionyl chloride and toluene, lower conversions to benzoyl chloride were obtained than in the absence of sulfur dioxide. Yet abundant sulfur dioxide is required for conversion of benzotrichloride to benzoyl chloride,[1] showing that side-chain chlorination by thionyl chloride is retarded by sulfur dioxide. Very likely, side-chain chlorination is caused by the chlorine liberated in the equilibrium 6, and the added sulfur dioxide shifts that equilibrium to the left. Consequently, the best conditions for the toluene to benzoyl chloride conversion involved first heating toluene and thionyl chloride at about 220 °C in glass for 2 h, followed by cooling, venting the hydrogen chloride formed, adding sulfur dioxide, and reheating. It is a "one-bomb" reaction.

$$4SOCl_2 \rightleftharpoons 3Cl_2 + 2SO_2 + S_2Cl_2 \qquad (6)$$

Molecules like m- and p-toluyl chloride are readily converted by thionyl chloride to dichlorotoluyl chlorides, but the last hydrogen is difficult to replace. This difficulty was circumvented by adding molecular oxygen to the bomb before heating. For example, dichloro-m-toluyl chloride[7] was heated for 4 h at 240 °C with (a) 3 mol of sulfur dioxide alone, (b) sulfur dioxide (3 mol) and oxygen (0.25 mol), and (c) sulfur dioxide (3 mol), oxygen (0.25 mol), and thionyl chloride (1 mol). The yields of distilled isophthaloyl chloride were 20, 50, and 88%, respectively. 2,6-Dichlorobenzal chloride was heated at 230–240 °C for 6–8 h with (d) sulfur dioxide (3.3 mol) and oxygen (0.25 mol), (e) sulfur dioxide (1.0 mol) and thionyl chloride (1.67 mol), and (f) sulfur dioxide (1.0 mol), thionyl chloride (1.67 mol), and oxygen (0.25 mol). The yields of distilled 2,6-dichlorobenzoyl chloride were 10, 15, and 34%, respectively. In case e, the major product was 1,2,3-trichlorobenzene. A mixture of tetrachloro- and pentachloro-m-xylene, when heated at 245 °C for 5 h with 12 mol of sulfur dioxide and 0.25 mol of oxygen, furnished a quantitative yield of isophthaloyl chloride. However, oxygen addition is not a panacea for high yields, since it caused increased tar formation with benzal chloride, toluene, and o-xylene.

The *o*-Xylene Problem. Commercial *m*-xylene available during the period of this research was typically 96–98% pure, the balance being roughly equal amounts of *o*- and *p*-xylene, sometimes with a little ethylbenzene as well. Photochlorination of this mixture formed HCMX containing 1–2% of the para isomer, and 1–2% of *penta*chloro-*o*-xylene (PCOX).[4] The para isomer is no serious problem; it can be separated from hcmx by fractional distillation or carried through to yield isophthaloyl chloride containing 1–2% of terephthaloyl chloride, which is an acceptable impurity for many uses. This is not true of PCOX, however. Its removal by fractionation is impractical, and dichloro-*o*-toluyl chloride would be a monofunctional chain stopper in polymer formation. The fate of PCOX in the various reactions which convert HCMX to IPC was therefore determined.

PCOX is hydrolyzed by water with Lewis acid catalyst to dichloro-*o*-toluyl chloride or further to 3-chlorophthalide. PCOX reacted with sulfur dioxide (no catalyst) at 230 °C to give phthalic anhydride (46% isolated yield) and a liquid mixture containing also *o*-phthaloyl chloride and its cyclic pseudo isomer (3,3-dichlorophthalide), dichloro-*o*-toluyl chloride, and 3-chlorophthalide. In a separate experiment, *o*-phthaloyl chloride (equilibrium mixture) was converted to phthalic anhydride (34% yield) by sulfur dioxide at 230 °C. In the presence of antimony pentachloride (2.3 mol %), PCOX did not react at all with sulfur dioxide up to about 130 °C, and only slightly at 160 °C; note that HCMX reacts completely at 100 °C to form IPC.[1] Since IPC is readily separable from PCOX, the catalyzed sulfur dioxide reaction provides a convenient method of coping with the *o*-xylene problem to assure the absence of monoacid chlorides.

Phosphorus pentoxide[2] reacted with PCOX to yield 91% of phosphorus oxychloride, but the organic material was almost entirely undistillable tar.

Sulfur trioxide[2] reacted completely with PCOX in trichlorotrifluoroethane solvent only when 4 mol was used; the product was chiefly 3-chlorophthalide; pyrosulfuryl chloride was formed in high yield. With only 2 mol of sulfur trioxide, the product was a mixture of dichloro-*o*-toluyl chloride, its cyclic isomer 2,2,5-trichlorobenzo[*b*]-2,5-dihydrofuran, and equivalent amounts of 3-chlorophthalide and unchanged PCOX.

Experimental Section

The same 240-ml shaker bomb, lined with Hastelloy C, was used in all the runs described. The organic substrate and the thionyl chloride were charged to the bomb which was sealed and pressure tested. It was then chilled to −80 °C and evacuated. The required amount of sulfur dioxide was added as described previously.[1] When oxygen was used, it was then added at −80 °C to give 200 psi pressure. The bomb was then heated with shaking. About 1 h was required to reach the operating temperature. When a range of temperatures is given in Table I, the bomb was held at the first temperature for about 1 h, and then slow heating raised the temperature to the second value in 2–3 h. Nickel powder, etc., was added before the bomb was sealed. After the hold period, the bomb was allowed to cool (about 1 h to 100 °C), and left overnight. The bomb was then vented and discharged, and the product was distilled. Thionyl chloride and sulfur monochloride were removed at atmospheric pressure, and the residue was then distilled rapidly at reduced pressure to separate the acid chloride from tar. The distillate was analyzed by GC as described previously.[1] The yield figure in Table I was calculated as if the distillate were pure ArCOCl; multiplying that number by the purity gives the true yield. ArCOCl is easily separated from $ArCCl_3$, when desired.

The sixth experiment in Table I was performed by loading the toluene and thionyl chloride into a glass liner which was then inserted into the metal autoclave. After the mixture had been heated at 220 °C for the first 2 h, the bomb was cooled and vented, and the sulfur dioxide was then added as described.[1] The bomb was reheated, held for 1 h at 200 °C, cooled, discharged, and distilled as described. Though this procedure gives good results, it is cumbersome. Normally it was preferred to add the sulfur dioxide initially, thus accepting the penalty of slower reaction.

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.—Thionyl chloride, 7719-09-7; sulfur dioxide, 7446-09-5.

References and Notes

(1) Part 1: C. S. Rondestvedt, Jr., *J. Org. Chem.*, accompanying paper in this issue.
(2) Part 2: C. S. Rondestvedt, Jr., *J. Org. Chem.*, preceding paper in this issue.
(3) See footnote 7 to ref 1 for a discussion of nomenclature and abbreviations used in this series of papers. See also footnote 13 for a list of patent disclosures of this work.
(4) J. Pollak and Z. Rudich, *Monatsh. Chem.*, **43,** 209 (1922), and papers cited therein.
(5) C. S. Rondestvedt, Jr., U.S. Patents 3 681 452; 3 681 453.
(6) R. B. Sandin, *Chem. Rev.*, **32,** 259 (1943).
(7) In this paragraph, the molar quantities given mean moles per mole of substrate.