nol: mp 40° (lit. mp 43°);[10] NMR (CCl_4) δ 1.60 (s, 12 H, CH_3), 1.78 (s, 6 H, CH_2).

2,6-Dibromo-2,6-dimethylheptane. 2,6-dimethyl-6-hydroxy-2-heptane (5 g) was cooled to −78° in CH_2Cl_2 (50 ml). HBr was bubbled into the solution for a total of 3.5 hr. The mixture was extracted with water (50 ml) and dried with K_2CO_3 and the solvent was removed. A 100% yield of 2,6-dibromo-2,6-dimethylheptane resulted which was recrystallized from ethanol: mp 34° (lit. mp 34°);[11] NMR (CCl_4) δ 1.90 (s, 12 H, CH_3), 1.90 (s, 6 H, CH_2).

Alkylation Experiments. A solution of the appropriate halide (0.2 *M*) in CH_3Cl was added to an equal volume of the trialkylaluminum (0.4 *M*) in CH_3Cl. Periodically, 5-ml samples were withdrawn and quenched with 1 ml of cold methanol. Saturated aqueous $KNaC_4H_4O_6$ was added to the samples and the organic layer was extracted into CCl_4 and dried with K_2CO_3. The samples were analyzed by GC, mass chromatography, and NMR,. The extent of alkylation was followed by NMR spectroscopy by determining the decrease in intensity of the methyl protons adjacent to the tertiary chlorine and tertiary bromine in the starting materials.

Final Hydrocarbon Products. 2,2,4,4-Tetramethylpentane resulting from the methylation of 2-bromo-4-chloro-2,4-dimethylpentane was identified by NMR and GC by comparison with an authentic sample (Chemical Samples Co.). 2,2,6,6-Tetramethylheptane[12] was identified by NMR and molecular weight: NMR (CCl_4) δ 0.93 (s, 18 H, CH_3), 1.15 (s, 6 H, CH_2). Calcd for $C_{11}H_{24}$: mol wt, 156.3. Found: mol wt, 155. Final products resulting from the reaction of Et_3Al and Et_2AlCl with 2-bromo-6-chloro-2,6-dimethylheptane (Table I) were analyzed by mass chromatography. Calcd for $C_{13}H_{28}$ (3,3,7,7-tetramethylnonane): mol wt, 184.4. Found: mol wt, 183. Calcd for $C_{11}H_{24}$ (2,6,6-trimethyloctane): mol wt, 156.3. Found: mol wt, 154. Calcd for C_9H_{20} (2,6-dimethylheptane[13]): mol wt, 128.29. Found: mol wt, 128. No other products were observed by gas chromatography.

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Registry No.—$AlEt_3$, 97-93-8; $AlEt_2Cl$, 96-10-6; $AlMe_3$, 75-24-1; 2-bromo-4-chloro-2,4-dimethylpentane, 54191-86-5; 2,4-dimethyl-4-hydroxy-1-pentene, 19781-53-4; methallyl chloride, 563-47-3; acetone, 67-64-1; 4-chloro-2,4-dimethyl-1-pentene, 54166-29-9; 2,6-dimethyl-6-hydroxy-2-heptene, 6090-15-9; 6-chloro-2,6-dimethyl-2-heptene, 6076-48-8; 2,6-dichloro-2,6-dimethylheptane, 35951-36-1; 2,6-dibromo-2,6-dimethylheptane, 54166-30-2; 2,2,6,6-tetromethylheptane, 40117-45-1; 3,3,7,7-tetramethylnonane, 54166-31-3; 2,6,6-trimethyloctane, 54166-32-4; 2,6-dimethylheptane, 1072-05-5; 2-chloro-6-bromo-2,6-dimethylheptane, 54166-33-5.

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Diacylium Cations from Tetrahaloterephthalic Acids and Their Electrophilic Reactivity

James O. Knobloch* and Fausto Ramirez

Research and Development Department, Amoco Chemicals Corporation, Naperville, Illinois 60540

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Diacylium bis bisulfate complexes are prepared from the reaction of sulfur trioxide with tetrabromoterephthalic acid, Br_4TA, and tetrachloroterephthalic acid, Cl_4TA. The spectra of the diacylium cations in the ultraviolet, visible, and infrared regions can be determined in SO_3–SO_2 and in SO_3–Freon 113 solvents. The diacylium complexes are excellent reagents for laboratory and industrial syntheses of diacid chlorides, diamides, and diesters of tetrahaloterephthalic acids; these products are obtained from the reactions of the complexes with chlorosulfonic acid, sulfamic acid, and alcohols, respectively. The diacylium complexes react with tetrahaloterephthalic acids to produce homopolymers and heteropolymers with an anhydride backbone. The perhalo polyanhydrides are stable at relatively high temperatures and are quite resistant to hydrolysis.

The extensive research of Olah and his coworkers[1] on stable oxocarbonium ions has demonstrated the possibility of generating diacylium cations from the acid fluorides of dicarboxylic acids. Thus, glutaryl fluoride and higher aliphatic diacid fluorides, as well as terephthaloyl fluoride, form 1:2 complexes with SbF_5 which have been formulated as diacylium bis(hexafluoroantimonate) salts, $SbF_6{}^{-+}OC(CH_2)_xCO^{+-}SbF_6$, on the basis of ir and NMR spectral data.

Diacylium cations have not, so far, been generated from dicarboxylic acids; however, monoacylium cations have been prepared from monocarboxylic acids by Deno and his coworkers.[2-4] These authors emphasized the potential value of such species in organic syntheses.

This paper describes the formation of diacylium cations from tetrahalogenated terephthalic acids, and from the corresponding terephthaloyl fluorides, $YCOC_6X_4COY$ (X = Br or Cl and Y = OH or F). The preparation of the diacylium cations from the reaction of SO_3 with tetrabromoterephthalic acid, Br_4TA, and with tetrachloroterephthalic acid, Cl_4TA, is economic and useful since the relatively stable dications serve as intermediates for the large-scale syntheses of acid chlorides, amides, nitriles, esters, and polyanhydrides derived from tetrahaloterephthalic acids. This type of dicarboxylic acid is notable for its lack of reactivity, as has been pointed out by several investigators.[5-7] The new perhalopolyanhydrides reported here are stable substances at relatively high temperature and are also quite resistant toward alkaline hydrolysis.

Results and Discussion

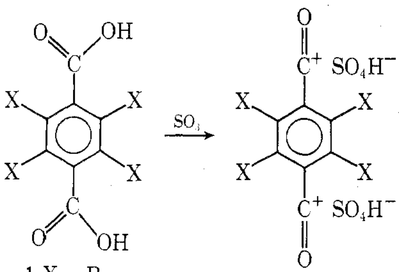
Spectrophotometric Detection of Diacylium Cations from the Reaction of Tetrahaloterephthalic Acids with Sulfur Trioxide. The Br_4TA (1) is soluble in a mixture of SO_3 and SO_2 in 85:15 wt % proportion. The resulting red solution has absorption maxima in the infrared, ultraviolet, and visible regions of the spectrum as shown in Table I. These data are consistent with the diacylium bis

Table I
Absorption Characteristics of Diacylium Complexes and Related Compounds

Compd	Solvent	Reagent	Ultraviolet and visible spectra		Infrared absorption frequencies, cm^{-1}
			λ_{max}, mμ	Molar absorptivity	
Tetrabromoterephthalic acid–sulfur trioxide complex	85% SO_3 15% SO_2	SO_3	541 432	1.4×10^3 6.2×10^{3b}	CO^+ 2243[c]
Tetrabromoterephthalic acid–sulfur trioxide complex	SO_3–Freon 113	SO_3	445 (s) 326 (w)		
Tetrachloroterephthalic acid–sulfur trioxide complex	85% SO_3 15% SO_2	SO_3	503 413	7.6×10^3 7.0×10^{3b}	CO^+ 2249[c]
Tetrachloroterephthalic acid–sulfur trioxide complex	SO_3–Freon 113	SO_3	433 (s) 300 (w)		
Tetrachloroterephthaloyl fluoride					C=O 1843[d]
Tetrachloroterephthaloyl fluoride–antimony pentafluoride complex	Fluorolube mull	SbF_5			CO^+ 2243
Terephthaloyl fluoride[a]	Fluorolube mull				C=O 1812
Terephthaloyl fluoride–antimony pentafluoride complex[a]	Fluorolube mull	SbF_5			CO^+ 2262

[a] Reference 1. [b] The apparent difference in molar absorptivities are due to deviations from Beer's law as they extrapolate to a common value at infinite dilution. [c] SO_3 solvent between thin Teflon sheets. [d] In KBr disk.

bisulfate structure **3**. Note, in particular, the $^+C{=}O$ absorption in the ir at 2243 cm^{-1}. Olah and Comisarow[1] assigned to the $^+C{=}O$ group the absorption band at 2262 cm^{-1} found in the ir spectrum of the complex obtained from the reaction of SbF_5 with the unsubstituted terephthaloyl fluoride.

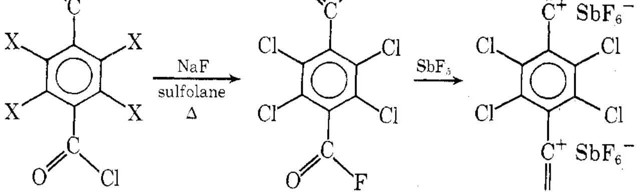


1, X = Br
2, X = Cl

3, X = Br
4, X = Cl

Tetrachloroterephthalic acid (**2**) responds in the same manner as Br_4TA in the SO_3–SO_2 solvent. The spectra of the orange-yellow solution of the diacylium cation **4** are summarized in Table I. The $^+C{=}O$ absorption is at 2249 cm^{-1}.

In order to obtain additional evidence on the structure of the species derived from the reaction of the tetrahalo diacids with SO_3, tetrachloroterephthaloyl fluoride (**7**) was treated with antimony pentafluoride in Freon 113[1] to form the hexafluoroantimonate salt, **8**. This salt can be isolated as an orange solid, mp 86–87°; the ir spectrum in a Fluorolube mull has a band at 2243 cm^{-1}.



5, X = Br
6, X = Cl

7

8

The tetrabromoterephthaloyl fluoride could not be prepared from the reaction of the corresponding chloride, **5**, with NaF, owing to halogen scrambling under the conditions required for the substitution of chloride by fluoride.

The addition of SO_3 to the Br_4TA (**1**) and the Cl_4TA (**2**) in the absence of SO_2 produces a suspension of the corresponding diacylium bis bisulfates, **3** and **4**. The ir spectra of the solid and the solution phases, examined within a thin Teflon envelope, show the bands of the diacylium cations. Dilution of the respective SO_3 phases with Freon 113 results in solutions with the uv spectra listed in Table I. There are significant differences between these uv spectra and the corresponding spectra of solutions of the diacylium cations, **3** and **4**, in the SO_3–SO_2 solvent. Two explanations seem possible for these differences. (a) The concentration of the salts, **3** and **4**, in the SO_3–Freon solvent is too low for observation of the weaker long-wavelength maxima (541 and 503 mμ, respectively). (b) In the solvent of lower polarity, the equilibrium which generates the diacylium bis bisulfates, **3** and **4**, from the monoacylium monosulfates, **3a** and **4a**, is shifted toward the monosulfates.

$$\mathbf{3} \text{ or } \mathbf{4} \rightleftharpoons HSO_4^- \;\; O{=}\overset{+}{C}C_6X_4CO_2H + SO_3$$

3a, X = Br
4a, X = Cl

From the spectroscopic data it can be concluded that the diacylium bis bisulfates, **3** and **4**, can be obtained either as a solution in SO_3–SO_2 solvent or as a solid. The solid salt, **3** or **4**, can be kept as a suspension in excess SO_3, or it can be freed from the SO_3 by extraction of the latter into Freon 113, or by vacuum distillation.

Reactions of the Tetrahaloterephthaloyl Diacylium Complexes with Nucleophiles. The reaction of the diacylium salts, **3** and **4**, with chlorosulfonic acid constitutes an excellent procedure for making the corresponding tetrahaloterephthaloyl chlorides, **5** and **6**.

$$\mathbf{3},\ \mathbf{4} + 2ClSO_3H \longrightarrow \mathbf{5},\ \mathbf{6} + 2H_2S_2O_7$$

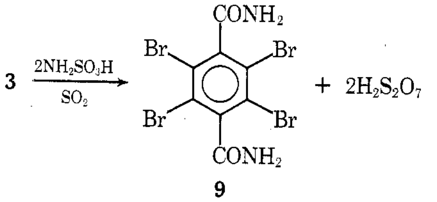
The tetrabromodiacylium bis bisulfate salt, **3**, can be treated with sulfamic acid in liquid SO_2 and this constitutes an excellent synthesis of tetrabromoterephthaldiamide (**9**).

Dialkyl esters of Br_4TA (**1**) and of Cl_4TA (**2**) are readily made from the diacylium salts, **3** and **4**, and the corresponding alcohols. As emphasized in the Experimental Sec-

Table II
Homopolymerization of Tetrabromoterephthalic Acid by Sulfur Trioxide without Preforming the Diacylium Complex

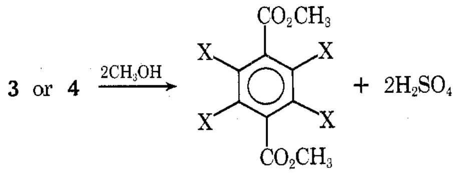
Br_4TA, g	SO_3, g	SO_2, g	SO_3/Br_4TA mole ratio	Polyanhydride yield, g (mol %)	Acid no., mg KOH/g	Average molecular weight	No. of Br_4TA units per polymer chain
15	2.5	139	1:1	9.9 (69)	10.8	10,400	22.4[a]
5.8	1.9	133	2:1	3.3 (59)	11.2	10,030	21.6
5.8	3.8	130	4:1	1.3 (23)	12.3	9,140	19.7

[a] Anal. Calcd for $C_8O_3Br_4$: Br, 68.9. Found: Br, 68.4.



9

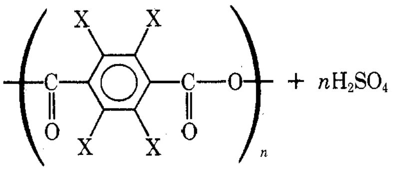
tion, the complete formation of the salts, 3 and 4, from the acids, 1 and 2, and SO_3 is aided by increasing the temperature or extending the reaction time.



10, X = Br
11, X = Cl

Homopolymerizations and Heteropolymerizations of Tetrahaloterephthalic Acids via Diacylium Complexes. The solid tetrabromodiacylium bis bisulfate salt, 3, prepared by the Freon-extraction method, reacts with Br_4TA in SO_2 in the temperature range 120–130° to give a tetrabromoterephthalic acid polyanhydride, 12. The structure of the polyanhydride 12 rests on infrared data, elemental analysis, and acid number derived by titration of acidic end groups with alkali. The tetrabromopolyanhydride 12 is obtained in 96.5 mol % yield, and the average polymer chain contains 21.4 monomer units.

$\frac{n}{2}$ 3 or 4 + $\frac{n}{2}$ 1 or 2 $\xrightarrow{SO_2}$



12, X = Br
13, X = Cl

The same type of polyanhydride, 12, is formed, although only in 68.5 mol % yield, if the tetrabromodiacylium salt, 3, is heated in SO_2, *in the absence of additional Br_4TA (1)*. This suggests that the following equilibria are established in SO_2; in this manner, the nucleophilic Br_4TA becomes available to react with the electrophilic diacylium cation. The counterion in the polymer would then be pyrosulfate.

$$3 \rightleftharpoons 3a \rightleftharpoons 1$$
$$SO_4H^- + SO_3 \rightleftharpoons S_2O_7H^-$$

A tetrabromopolyanhydride, 12, of about the same average molecular weight can also be made by the addition of stoichiometric amounts of SO_3 to Br_4TA (1) in SO_2, followed by heating to ca. 125°. This procedure generates the diacylium cation in situ. The results of such an experiment, with the mole ratio $SO_3/Br_4TA = 1$, are shown in Table II; note that the average polymer molecule contains 22.4 monomer units, although the yield has dropped to 69 mol %. Some polyanhydride is still produced at a mole ratio $SO_3/Br_4TA = 2$ and even at $SO_3/Br_4TA = 4$, although no polymer should have been produced if bisulfate, SO_4H^-, were the only possible counterion. In that case no nucleophilic carboxylic acid groups would have been present. Again the results suggest the formation of pyrosulfate anions, $S_2O_7H^-$, and anions of higher SO_3 content.

$$n HO_2CC_6X_4CO_2H \xrightarrow[SO_2]{+nSO_3} \textbf{12 or 13}$$

The solid tetrachlorodiacylium bis bisulfate salt, 4, formed in the Freon-extraction method, reacts with Cl_4TA in SO_2 solvent at about 125° to give a tetrachloroterephthalic acid polyanhydride, 13, of relatively low average molecular weight, 3300 (or 11.5 Cl_4TA units per polymer chain). On the other hand, Cl_4TA (1 mol) is polymerized by SO_3 (1 mol) in SO_2 solution at about the same temperature, but without isolation of the solid tetrachlorodiacylium complex, to give a tetrachloropolyanhydride of relatively high molecular weight, 8640 (or 30.1 Cl_4TA units per polymer chain).

Heteropolymeric anhydrides can be made from the reaction of solid tetrabromodiacylium bis bisulfate complex (3) with Cl_4TA, and by the reaction of solid tetrachlorodiacylium bis bisulfate complex (4) with Br_4TA, both in SO_2 medium. The polymer from 1 mol of tetrabromodiacylium complex and 2 mol of Cl_4TA has a 1:1.83 molar proportion of $C_8O_3Br_4$:$C_8O_3Cl_4$, with an average molecular weight of 3500, and an average of 3.5 tetrabromo- and 6.5 tetrachloroterephthalic acid units per polymer chain. The polymer represents a 47 mol % yield from Br_4TA and a 43 mol % yield from Cl_4 TA.

The polymer made from 1 mol of tetrachlorodiacylium complex and 1 mol of Br_4TA has a 1:1.37 molar proportion of $C_8O_3Cl_4$:$C_8O_3Br_4$, with an average molecular weight of 4677, and an average of 5.06 tetrachloro- and 6.93 tetrabromoterephthalic acid units per polymer chain. The polymer represents a 49 mol % yield from Cl_4TA and a 67 mol % yield from Br_4TA.

The perhalopolyanhydrides made available by the diacylium cation method are interesting materials. They are extremely resistant to hydrolysis, and prolonged digestion in boiling water causes no appreciable decomposition. Indeed, a sample of Br_4TA polyanhydride kept 15 days in contact with boiling aqueous potassium hydroxide (3 equiv of KOH per acid equivalent) shows no significant changes in the ir spectrum; no Br_4TA is obtained upon acidification of the alkaline extract.

In general, the yield of polyanhydride is lower from Cl_4TA than from Br_4TA. Moreover, the average chain length varies with the procedure used for Cl_4TA, but not

Table III
Partial Mass Spectra of $ClCOC_6X_4COCl$ Doubly Charged Ions

	Rel intensities,[a] X		
Ion composition[b]	H	Cl	Br
M ≡ Diacid chloride	0	0.2	Trace
M − Cl[c]	0	0.7	0.4
M − (Cl + CO)	0	1.2	0.4
M − 2Cl	8.8	23.5	29.8
M − (Cl + 2CO)	0	0.3	0.2
M − (2Cl + CO)	8.8	3.8	5.4
M − (2Cl + 2CO)	5.5	28.6	13.0

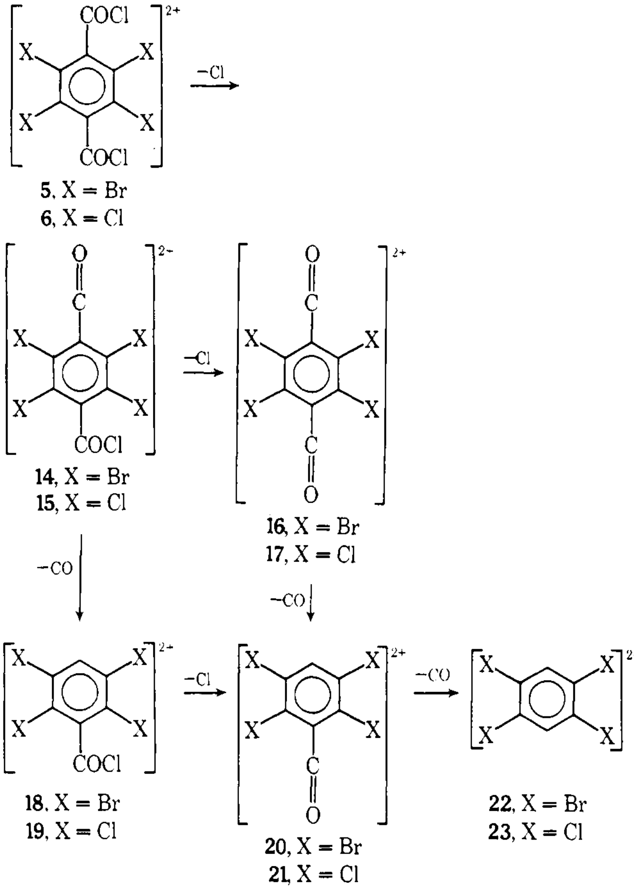
[a] Intensities are expressed on a scale defined by assigning a value of 100.0 to $[M - Cl]^+$, the most abundant ion species in each of the spectra. [b] The natural abundances of bromine and chlorine atoms result in multiplets of two or more peaks for each halogen-containing ion. The intensity profiles of such multiplets define the number and identities of the halogen atoms. The intensities of all the peaks in each such multiplet have been summed to arrive at the intensities shown in the table for the corresponding ion compositions. [c] The diacid chloride minus the indicated atom(s).

for Br_4TA. These differences may be related to the lower degree of stability of the chlorodiacylium vs. the bromodiacylium cations. The polymerization may occur by two different but related pathways when 1 mol of SO_3 is added to 1 mol of the tetrahalo acid. (1) The diacylium cation is formed, and this is followed by reaction with the free acid. (2) The monoacylium cation is formed and undergoes a head-to-tail polymerization. Regardless of the actual polymerization mechanism in the tetrahalo acid–SO_3–SO_2 procedure, there is no doubt that diacylium cations can be generated from the acids and SO_3, as shown by the spectral and the chemical evidence.

For comparison purposes the new tetrabromo diacid chloride, **5**, and the known tetrachloro diacid chloride,[6,7] **6**, were made also from the reaction of the corresponding acids, Br_4TA and Cl_4TA, with thionyl chloride. The mass spectra of these compounds and of terephthaloyl chloride are summarized in Table III. The data confirm the structures of the acid chlorides; moreover, the mass spectra indicate the relative probability with which the diacylium cation forms and survives intact in the vapor phase under electron impact. Note that for each of the three diacid chlorides a very intense peak for a doubly charged species corresponds to a process in which the two chlorine atoms have been removed from the diacid chloride. Furthermore, the doubly charged species is most abundant for the tetrabromo and least abundant for the unsubstituted diacid chloride, as would be expected from the relative stabilities of the diacylium cations.

For the tetrabromo and tetrachloro compounds, the important reactions involving the two acid chloride functional groups are shown in Scheme I. For tetrabromoterephthaloyl chloride (**5**) the loss of two chlorines forms **16** as the most abundant doubly charged species. The intensity of the species **22** from the subsequent loss of two carbonyl groups is less than half that of **16**. By contrast, tetrachloroterephthaloyl chloride (**6**) forms the doubly charged diacylium species, **17**, but this species is overshadowed by the greater relative intensity of **23**, the $C_6Cl_4^{2+}$ fragment.

Scheme I



These decompositions in the vapor phase seem to parallel the performance of the diacylium cations in homopolymerizations with the corresponding acids in liquid sulfur dioxide medium. Thus, the preformed diacylium bis bisulfate of Br_4TA reacted with Br_4TA to form the polyanhydride in 97 mol % yield. The corresponding homopolymerization of Cl_4TA formed the polyanhydride in only 43 mol % yield. Furthermore, the average Br_4TA polymer chain contains almost twice the number of monomer units as does the the Cl_4TA anhydride polymer.

If we assume that the more efficient reactivity of the Br_4TA diacylium ion is realized because of its greater stability until reaction with Br_4TA can occur, then a parallel exists with the relative intensities of the mass spectra.

Experimental Section

Tetrabromoterephthalic Acid (Br_4TA). The tetrabromoterephthalic acid (**1**, Br_4TA) was made from terephthalic acid by bromination in fuming sulfuric acid with iodine catalyst under conditions more severe than for tetrabromophthalic anhydride[8] or for 2,5-dibromoterephthalic acid.[9] Terephthalic acid (322 g) was dissolved in 3666 g of fuming sulfuric acid (20% SO_3, 80% H_2SO_4) by heating to 69° with stirring in a three-neck, 3-l. round-bottom flask equipped with a stirrer, thermometer, and condenser protected from atmospheric moisture by concentrated sulfuric acid in a gas bubbler. The flask was protected from light by an aluminum foil shield. Iodine (12.5 g) was added to the flask as the solution cooled to room temperature. Bromine (702 g) was added and the flask was heated to reflux (60°). After 76 hr the pot temperature had risen to 125° and the heat was turned off. The cooled suspension was filtered on a fritted glass Buchner funnel. The filter cake was washed with 200 ml of concentrated sulfuric acid. The acid wet cake digested on the steam bath in 2 l. of water for 30 min. After cooling, the insoluble acid was filtered, washed on the filter successively with 700 ml of 10% hydrochloric acid and 400 ml of distilled water, and dried. The dry cake weighed 768.3 g. Its neutral equivalent was 245 and it contained 65.7% bromine. A sample was esterified with diazomethane and analyzed by gas chromatography. It contained 96.8 area % Br_4TA, 2.0% hexabromobenzene, 0.30% Br_3TA, and 0.68% Br_2TA.

Part of this crude product (384 g) was dissolved in 2 kg of 5% sodium hydroxide solution and was filtered to remove insoluble hexabromobenzene. The filtrate was added to 320 g of 44% sulfuric acid at 65–75° to recover the organic acids. After filtration and washing with 600 ml of water, the cake was recrystallized from methanol. The purified tetrabromoterephthalic acid weighed 273 g. Anal. Calcd for $C_8H_2Br_4O_4$: Br, 66.35; neut equiv, 240.9. Found:

Br, 66.5; neut equiv, 241.0. The ir (KBr disk) showed 1734 (s), 1659 (s), 1546 (w), 1445 (w), 1400 (s), 1337 (s), 1310 (s), 1257 (s), 1235 (s), 1180 (w), 1090 (m), and 776 cm^{-1} (m). A sample of the acid was converted to dimethyl tetrabromoterephthalate with diazomethae. The ester had a melting point of 229°; the ir (KBr disk) showed 1734 (s), 1439 (m), 1386 (m), 1332 (m), 1304 (w), 1238 (s), 1184 (w), 1081 (m), 944 (m), and 829 cm^{-1} (w).

Tetrachloroterephthalic Acid (Cl_4TA). Tetrachloroterephthalic acid was made following a published procedure[10] except that the chlorination was carried out at atmospheric pressure. The filter cake was digested in water to remove occluded sulfuric acid. Finally the crude Cl_4TA was recrystallized from methanol. Anal. Calcd for $C_8H_2O_4Cl_4$: Cl, 46.67; neut equiv. 151.97. Found: Cl, 46.75, neut equiv, 152.0.

Tetrabromoterephthaloyl Chloride from Tetrabromoterephthalic Acid and Thionyl Chloride. A mixture of Br_4 TA (1.0 g) and thionyl chloride (56 g) was kept for 1 hr at reflux temperature. The solution was evaporated almost to dryness without overheating the residue, which was then treated with water (25 ml), stirred, and filtered to yield the crude acid chloride. The latter was purified by trituration with methanol (40 ml) at 25° and drying at 60° under vacuum. Tetrabromoterephthaloyl chloride (1.0 g) had mp 196.0–196.5°, and ir bands (KBr disk) at 1850 (w), 1770 (s), 1318 (s), 1115 (s), and 870 cm^{-1} (s). Further characterization by mass spectrometry appears in Table III.

Tetrachloroterephthaloyl Chloride from Tetrachloroterephthalic Acid and Thionyl Chloride. A similar procedure gave tetrachloroterephthaloyl chloride: mp 145.5–146.0°; ir bands (KBr disk) at 1775 (s), 1355 (s), 1165 (s), 902 (s), and 890 cm^{-1} (s). The literature reports mp 144–145[7] and 147.5–148°,[11] and a comparable ir spectrum.

Preparation of Tetrachloroterephthaloyl Fluoride. The procedure of Tullock and Coffman[12] was satisfactory for the preparation of tetrachloroterephthaloyl fluoride. The reactants were heated for 1.5 hr at 215–226°. The product codistilled with the tetramethylene sulfone under vacuum (115° pot temperature, 1 mmHg), from which it was separated by dilution with water. This compound, after recrystallizing from a benzene-*n*-heptane solution, melted at 138.8–140.3° (lit.[13] mp 138.°). The ir spectrum (KBr) showed a strong carbonyl absorption at 1843 cm^{-1}.

Reaction of Tetrachloroterephthaloyl Fluoride with Antimony Pentafluoride. This reaction was carried out in 1,1,2-trifluorotrichloroethane (Freon 113) solution at 25° for 15 min, otherwise following the procedure of Olah and Comisarow[1] for the generation of the diacylium bis(hexafluoroantimonate) from terephthaloyl fluoride. The diacylium bis(hexafluoroantimonate) that precipitated from the solvent on adding a Freon solution of tetrachloroterephthaloyl fluoride to the Freon-diluted SbF_5 was reddish orange and had the ir spectrum shown in Table I.

Spectrophotometric Detection of the Diacylium Complexes Generated from the Reaction of Tetrahaloterephthalic Acids with Sulfur Trioxide. A. Spectra in 85:15 wt % SO_3:SO_2. Samples of the acids were weighed into volumetric flasks and made up to volume with a mixture of 85 wt % sulfur trioxide and 15 wt % sulfur dioxide. The solution from the tetrabromo acid was red, and the solution from the tetrachloro acid was yellow. The spectra were determined in the visible region, in quartz cells, in a Cary 16 spectrophotometer. The data are given in Table I.

B. Spectra in SO_3–Freon 113. Samples of the acids (0.3 g), Br_4TA and Cl_4TA, respectively, were triturated for 1 min with liquid sulfur trioxide (2.5 ml) in a dry nitrogen atmosphere. The corresponding suspension was diluted with Freon 113, and the clear supernatant solution was further diluted with appropriate volumes of Freon 113 for the determination of the spectra in the uv and visible regions, in quartz cells, in a Cary 14 spectrophotometer. See Table I.

Precautionary Note. Sulfur trioxide reacts vigorously with carbon tetrachloride to give phosgene and pyrosulfuryl chloride:[14] $2SO_3 + CCl_4 \rightarrow COCl_2 + ClSO_2OSO_2Cl$. Therefore, most of the SO_3 must be removed before CCl_4 is added as solvent in the following reactions. Furthermore, excessive amounts of pyrosulfuryl chloride render $ClSO_3H$ and CCl_4 miscible, and thus prevent the extraction of tetrachloroterephthaloyl chloride by CCl_4 from a mixture of the chloride and $ClSO_3H$.

Generation of Diacylium Complex from Tetrabromoterephthalic Acid and SO_3 and Reactions of the Complex with Nucleophiles. A. Reaction with Chlorosulfonic Acid. Tetrabromoterephthalic acid (1.0 g) was dissolved in sulfur trioxide (33 ml), with stirring, in a round-bottomed flask. The deep red solution became yellow as a dense layer separated from the main SO_3 solution. The mixture of two layers was distilled, first at 370 mm, and finally at 300 mm, at a bath temperature of 46°. To the residue from the distillation (6.7 g) was added chlorosulfonic acid (15 ml), and the mixture was kept at ambient temperature overnight. The contents of the flask were transferred to a separatory funnel by means of CCl_4 (30 ml), and the lower $ClSO_3H$ layer was separated and extracted further with two 20-ml portions of CCl_4. The combined CCl_4 extracts were evaporated at atmospheric pressure. The residue (5.7 g) was transferred to a sublimator (Kontes No. 5880), modified to carry the vapors to a cold receiver through an all-glass line. With the bath at 132°, the pressure at 10 mm, and steam passing through the condenser, the $ClSO_3H$ (4.6 g) that had been dissolved in the product was transferred to the cold receiver. With the bath at 280°, the pressure at 10 mm, and cold water passing through the condenser, tetrabromoterephthaloyl chloride (0.4 g) sublimed to the cold surface. The chloride melted at 199.5–200.5°; gas chromatography showed 99.9 area % purity.

A mass spectrum (low voltage) of the chloride was made by direct probe introduction, subjecting the sample to microdistillation in the instrument. Only one large peak was seen by the beam current signal, exhibiting maximum abundance in the vapor phase with the source and probe both at about 250°. The six spectra measured under this peak were identical except for intensity, and confirm the structure as $C_8Br_4Cl_2O_2$. The doubly charged ion $O{=}C^+C_6Br_4{}^+C{=}O$ was observed.

B. Reaction with Sulfamic Acid. A 3.5-g sample (7.26 mmol) of tetrabromoterephthalic acid was treated, under dry nitrogen, with 25 ml of sulfur trioxide in an open 300-ml Hastelloy C autoclave. After 8 min of stirring, 100 ml of Freon 113 was added to dissolve excess SO_3. The suspension was stirred and the clear liquid was decanted from the sticky solids in the vessel. Two 50-ml portions of Freon 113 were used to remove the remaining SO_3. Sulfamic acid (2.8 g, 29 mmol) was added to the autoclave, which was then closed and pressure tested with N_2; after venting, 130 g of sulfur dioxide was introduced from a tared cylinder. The temperature was raised to 108° (45 min, stirring at 2000–2400 rpm) and was held at 108–116° for an additional 100 min (pressure 450–485 psig) with stirring. The reactor was kept overnight at 23° (pressure 65 psig), and then was cooled in a Dry Ice–2-propanol bath and opened. After SO_2 evaporation, the residue was digested at 90° in 550 ml of water, cooled in an ice bath, filtered, and dried (50°, under vacuum) to yield 3.0 g of crystalline residue. This was refluxed in methanol to extract Br_4TA and leave insoluble 1.5 g of tetrabromoterephthaldiamide (mp ca. 342° dec). The ir spectrum (KBr disk) had bands at 1675 (s), 1595 (w), 1330 (m), 1305 (w), 1230 (m), 1120 (w), and 1080 cm^{-1} (w); the ir spectrum in Nujol mull showed the bands at 3442 and 3250 cm^{-1} for the NH_2 group. Microdistillation in the mass spectrometer showed one big peak due to tetrabromoterephthalodinitrile resulting from the dehydration of the diamide. Additional very weak peaks occurred at the diamide and the amide–nitrile masses.

C. Reaction with Methanol. Tetrabromoterephthalic acid (4.0 g) was suspended in 396 g of SO_3 and brought to a boil with stirring over a 1-hr period. A golden lower liquid layer developed. After cooling to 25° the upper sulfur trioxide phase was decanted, leaving 17.5 g of "underlayer". This layer was washed four times by suspending in 50-ml portions of Freon 113 and decanting to remove dissolved sulfur trioxide. The washed underlayer, which weighed 7.6 g, was added to 425 ml of absolute methanol with stirring. About 300 ml of methanol was distilled and the residual solution was cooled to 25°. A crystalline solid product was recovered by filtration. The filter cake was washed with 10 ml of methanol and dried to give dimethyl tetrabromoterephthalate (1.8 g, mp 207–210°); ir confirmed the identity of the diester. A gas chromatogram showed only one peak at the correct retention time.

In another experiment, 3.3 g of Br_4TA was similarly boiled in 50 ml of SO_3 and then cooled to room temperature. The upper SO_3 layer was decanted, and the golden underlayer was heated under vacuum for 30 min to a bath temperature of 56° to remove SO_3. To the residue (6.5 g), 35 ml of absolute methanol was added through a reflux condenser (vigorous reaction). After refluxing for 30 min, the suspension of white solids was cooled to room temperature, poured into 100 ml of water, digested on the steam bath, cooled, and filtered. The 2.5 g of dry solids was partitioned between chloroform and 5% sodium bicarbonate solution. On evaporation of the chloroform, 1.13 g of dimethyl tetrabromoterephthalate was recovered (mp 224.5°). The correct ir spectrum was obtained.

Generation of Diacylium Complex from Tetrachloroterephthalic Acid and SO_3, and Reaction of the Complex with Nucleophiles. A. Reaction with Chlorosulfonic Acid. Tetrachloroterephthalic acid (3.0 g) was dissolved in sulfur trioxide (150 ml), and the mixture was stirred for 1 hr at 25° in a closed flask. The initial orange solution turned pale yellow after the separation of a heavy layer (15 min). The excess SO_3 was distilled at 44–46° and atmospheric pressure (70° bath), and the residue was treated with chlorosulfonic acid (25 ml) and stirred for 90 min at ambient temperature. The mixture was extracted with five 50-ml portions of CCl_4, the combined extracts were evaporated, and the residue was sublimed as in the case of the bromo analog (bath temperature 190–204°, pressure 1 mm, time 50 min). Tetrachloroterephthaloyl chloride (2.0 g, mp 144.5–146.5°) was identified by comparison with a sample made from the acid and thionyl chloride.

In an identical experiment, except that the excess SO_3 was removed by dilution with Freon 113, decantation, and subsequent extraction of the solids with additional Freon, 2.1 g of tetrachloroterephthaloyl chloride was obtained.

B. Reaction with Methanol. Tetrachloroterephthalic acid (0.9 g) was added to 86 g of SO_3 in a covered erlenmeyer flask. The bright yellow suspension was heated and after 15 min became cloudy yellow with green solids out of solution. After 1 hr (about 20 min at boiling) the suspension was allowed to cool to room temperature. The yellow SO_3 upper layer was decanted from the greenish yellow solids, which were then cautiously added to methanol and allowed to stir. A crystalline product that precipitated from solution was filtered off, shaken with water, and dried to give dimethyl tetrachloroterephthalate (0.3 g), mp 152–154.5° (lit.[7] mp 154–155°). The ir spectrum (KBr) was identical with that of the dimethyl ester made by the reaction of Cl_4TA with diazomethane.

Homopolymerizations via the Tetrabromoterephthaloyl Diacylium Complex. A. With Preformed Diacylium Complex. Tetrabromoterephthalic acid (2.5 g) and SO_3 (25 ml) were allowed to react for 1 min under N_2 in a 300-ml Hastelloy C autoclave. The excess SO_3 was removed by extraction with one 100-ml and three 50-ml portions of Freon 113. The residual diacylium complex was mixed with additional Br_4TA (3.0 g) in the autoclave, which was then closed and pressurized with SO_2 (136 g). The mixture was kept for 25 min at 120–129°, with stirring (1600 rpm). The autoclave was cooled in a Dry Ice–2-propanol bath and opened. The liquid phase was decanted from a solid residue, which was washed with three 20-ml portions of Freon 113, and dried in a vacuum at 50°. This residue was refluxed with boiling methanol (95 ml), cooled, filtered, and dried to give 5.1 g (96.5 mol % yield) of tetrabromoterephthalic acid polyanhydride (mp >400°). The ir spectrum (KBr disk) had strong bands at 1820, 1780, 1130, and 980 cm^{-1}. A sample of the polyanhydride was titrated in a methanol suspension, giving an acid number of 11.3 mg KOH/g. On the assumption that only free acid end groups are titrated, this corresponds to a molecular weight of 9950. A thermogravimetric analysis in air showed a 5 wt % loss at 355°, an additional 5 wt % loss at 376°, and a further 2 wt % loss at 400°.

In an analogous reaction, Br_4TA (2.7 g) was allowed to react with SO_3 (25 ml); however, no additional Br_4TA was added to the diacylium complex prior to heating in liquid SO_2. The polyanhydride was obtained in 68.5 mol % yield (1.8 g); its acid number was 10.9.

B. Without Isolation of Diacylium Complex. In a series of reactions, Br_4TA and a predetermined amount of SO_3 were added to a Hastelloy C autoclave, the SO_2 solvent was introduced, and the mixture was heated for 70 min at 120–123° (570–620 psig) with stirring (2200 rpm). The autoclave was then cooled and opened, and the liquid phase was decanted and allowed to evaporate. The residue and the solid product from the autoclave were suspended in water (45 ml/g Br_4TA charged), digested at 90°, cooled, and filtered; the solid was washed with two 35-ml portions of water and dried. The polyanhydride was refluxed with boiling methanol (16 ml/g of crude product) to remove any unreacted Br_4TA, dried, and analyzed. The results are shown in Table II.

Homopolymerizations via the Tetrachloroterephthaloyl Diacylium Complex. A. With Preformed Diacylium Complex. Tetrachloroterephthalic acid and SO_3 were allowed to react for 15 min as described for the bromo analog, except that the mixture of diacylium complex, additional Cl_4TA, and SO_2 was brought to 105° (at 430 psig) during 37 min, and was kept for 15 min at 105–108° and 30 min at 115–125° (516–615 psig). The tetrachloroterephthalic acid polyanhydride was isolated as in the case of the bromo analog. From 2.5 g of Cl_4TA, 25 ml of SO_3, an additional 3.0 g charge of Cl_4TA, and 126 g of SO_2, 2.22 g of purified polyanhydride was obtained. The acid number was 34 mg KOH/g. The ir spectrum (KBr disk) had bands at 1820 (s), 1763 (w), 1170 (s), and 1000 cm^{-1} (s).

B. Without Isolation of Diacylium Cation. The Cl_4TA (9.45 g), SO_3 (2.5 g), and SO_2 (136 g) were allowed to react in the autoclave as described for the bromo analog. The autoclave was brought to 120° (576 psig) during 1 hr and was kept for 90 min at 123–129° (614–675 psig).

The chlorinated polyanhydride was isolated as in the case of the bromo analog. The yield of purified polyanhydride was 2.7 g; its acid number was 13 mg KOH/g. Anal. Calcd for $C_8O_3Cl_4$: Cl, 49.6. Found: Cl, 49.1.

Heteropolymerizations. A. Tetrabromoterephthaloyl Diacylium Complex with Tetrachloroterephthalic Acid. The bromodiacyl complex was made from Br_4TA (3.5 g) and SO_3 (25 ml) in 5 min, in an autoclave, as described above. After the excess SO_3 had been removed with Freon 113, the Cl_4TA (4.4 g) and the SO_2 (139 g) were added to the autoclave, which was heated for 70 min at 124–127° (622–648 psig). The tetrabromotetrachloroterephthalic acid polyanhydride (3.4 g) was isolated after purifying as in the case of homopolymers. The mixed polyanhydride had ir bands at 1820 (s), doublet 1785 and 1763 (both w), 1170 (s), 1145 (s), and 990 cm^{-1} (s). Elemental analysis gave 31.9% Br and 26.0% Cl, which corresponds to 46.3 wt % $C_8O_3Br_4$ and 52.4 wt % $C_8O_3Cl_4$. The acid number was 32 mg KOH/g.

B. Tetrachloroterephthaloyl Diacylium Complex with Tetrabromoterephthalic Acid. The chloro diacyl complex was made from Cl_4TA (2.20 g) and SO_3 (25 ml) in 5 min. The Br_4TA (3.49 g) and SO_2 (137 g) were introduced after the excess SO_3 had been removed by Freon 113 as described above. The autoclave was brought to 123° in 1 hr and was kept at 123–126° for 1.5 hr. The tetrachlorotetrabromoterephthalic acid polyanhydride (3.4 g) was isolated as described above. The ir spectrum had bands at 1820 (s), 1785 (s), 1763 (shoulder), 1173 (w), 1138 (s), and 990 cm^{-1} (s). Elemental analysis gave 14.7% Cl and 45.5% Br, which corresponds to 29.6 wt % $C_8O_3Cl_4$ and 66.0 wt % $C_8O_3Br_4$. The acid number was 24 mg KOH/g.

Attempted Alkaline Hydrolysis of the Polyanhydride of Tetrabromoterephthalic Acid. A 43.8-mg sample of the polyanhydride of Br_4TA was stirred at reflux in 100 ml of water containing 36.8 mg of potassium hydroxide for 15 days. The anhydride sample did not go into solution during this time. The cooled solution was filtered through a millipore filter, the filtrate was evaporated, and about 0.04 g of residue was recovered. An ir spectrum showed only H_2O and SiO_2. The filter cake had an ir spectrum essentially identical with that of the polyanhydride charged.

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Registry No.—**1**, 5411-7-1; **2**, 2136-79-0; **3**, 54120-53-5; **4**, 54120-55-7; **5**, 54120-56-8; **6**, 719-32-4; **7**, 652-35-7; **8**, 54120-57-9; **9**, 54120-58-0; **10**, 54120-51-3; **11**, 1861-32-1; **12**, 54181-85-0; **13**, 54120-59-1; terephthalic acid, 100-21-0; antimony pentafluoride, 7783-70-2; sulfur trioxide, 7446-11-9; chlorosulfonic acid, 7790-94-5; sulfamic acid, 5329-14-6; tetrabromoterephthalodinitrile, 54181-84-9; methanol, 67-56-1; tetrabromotetrachloroterephthalic acid polyanhydride, 54120-60-4.

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