Mixed Sulfonic–Carboxylic Anhydrides. I. Synthesis and Thermal Stability. New Syntheses of Sulfonic Anhydrides

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Two new high-yield syntheses of mixed sulfonic–carboxylic anhydrides are described. Two modes of thermal decomposition of the products, disproportionation to simple anhydrides, and ketene extrusion take place, relative rates being dependent upon the temperature of reaction. The disproportionation reaction is used to effect a general synthesis of sulfonic anhydrides, whose behavior toward heat is also studied.

Mixed sulfonic–carboxylic anhydrides, formally derived by elimination of one molecule of water from a carboxylic and a sulfonic acid, have in the past received very little attention, although known for over 35 years. While *o*-sulfobenzoic anhydride, readily prepared from the acid, has been known since 1889,[2] the more active aliphatic sulfonic–carboxylic anhydrides were first mentioned in 1933 when Baroni[3] allegedly prepared a series of such compounds by treating silver or sodium carboxylate salts with aromatic or aliphatic sulfonyl chlorides at temperatures of between 120 and 200° for up to 10 hr, the products being collected by distillation (20 mm). Since, however, the products themselves, as will be demonstrated, are unstable at such temperatures and pressures, the validity of this work must remain open to question. A more efficient and unambiguous synthesis was pioneered by Overberger and Sarlo,[4] who treated acetonitrile solutions of silver sulfonates with acyl halides obtaining the mixed anhydride in moderate yield. Other syntheses of mixed anhydrides involved the reactions of sulfonic acids with ketene[5] and of sulfonyl chlorides with aromatic carboxylic acids in pyridine.[6] However, the yields in the former case were no greater than 10%, while the latter appeared to be restricted to aryl acyl chlorides.

We have developed two simple alternative modes of synthesis of mixed sulfonic–carboxylic anhydrides utilizing sulfonic acid and either acyl chloride or anhydride. Concurrently we have utilized this new method to effect two new high-yield syntheses of sulfonic anhydrides which possess advantages of yield, simplicity of operation, and cost over the available syntheses.[7] It is with these syntheses and some aspects of the thermal behavior of the mixed anhydrides that the present paper is concerned. The chemistry of mixed sulfonic–carboxylic anhydrides has been alluded to briefly[8] and will be more extensively considered in further publications in this series.[9]

Synthesis *via* Acid Chloride.—The synthetic method of choice consists in reacting an excess of carboxylic acid chloride with a sulfonic acid (eq 1). The method appears quite general, the ease of reaction decreasing markedly with the increase in electronegativity of the group attached to the carbonyl group of the acid chloride. The reaction course is readily charted by observation of the HCl gas, evolved as the only other primary product. In general, aliphatic acid chlorides present no difficulty, reaction being conducted either in the acid chloride itself as solvent, or in benzene (whose reflux temperature of 80° proves convenient). Thus with acetyl chloride, evolution of HCl ceases after 3–5 hr. When reaction is complete the solvent, if any, and excess acid chloride are removed at reduced temperature and pressure. The residue contains the mixed anhydride. Table I lists the anhydrides prepared by this method. All these products were characterized by a strong single carbonyl stretching frequency between 1780 and 1820 cm^{-1} and by their nmr spectra, details of which are given (Table I).

$$\mathrm{RCOCl} + \mathrm{R'SO_3H} \longrightarrow \mathrm{RCOOSO_2R'} + \mathrm{HCl} \qquad (1)$$

$$\mathrm{R} = \mathrm{CH_3} = \mathrm{C_2H_5} = \mathrm{C_6H_5CH_2} = \mathrm{(CH_3)_2CH} = \mathrm{C_6H_5}$$
$$\mathrm{R'} = \mathrm{CH_3} = \mathrm{CH_3C_6H_4}$$

As prepared in this manner the products are contaminated by traces of free acid and by sulfonic anhydrides, the proportions of which were simply estimated from the nmr spectra. The presence of acid is due either to incomplete reaction, to thermal decomposition (*vide infra*), or to adventitious hydrolysis, to which the mixed anhydrides are exceedingly susceptible. The presence of sulfonic anhydride is the result of thermal disproportionation (*vide infra*). Purification by distillation is applicable only to the simplest member of the series, acetyl methanesulfonate, whose distillation temperature at 10^{-2} mm is sufficiently removed from the decomposition temperature as to enable almost quantitative recovery in analytically pure condition. All other mixed anhydrides suffered extensive decomposition upon attempted distillation. The products from aryl sulfonic acids are generally low-melting crystalline solids. Although purification by crystallization from hexane,[4,10] benzene, acetic anhydride,[11] or methylene chloride[6] have been reported for some of these compounds, we have found recrystallization to be unreliable as a means of purification, effecting partial hydrolysis. In general, mixed anhydrides could be used without further purification for most purposes.

When the acyl group is substituted by more electronegative groups, the reaction rate is correspondingly

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[1] Weizmann Fellow, 1967–1969.

[2] A. Fahlberg, *Chem. Ber.*, **22**, 757 (1889).

[3] A. Baroni, *Atti Accad. Naz. Lincei, Mem., Cl. Sci. Fis., Mat. Natur.*, **17**, 1081 (1933).

[4] C. G. Overberger and E. Sarlo, *J. Amer. Chem. Soc.*, **85**, 2446 (1963).

[5] G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **27**, 2667 (1962).

[6] H. Boehme and K.-H. Meyer-Dulheuer, *Justus Liebigs Ann. Chem.*, **688**, 78 (1965).

[7] L. Field, *J. Amer. Chem. Soc.*, **74**, 394 (1952); H. G. Khorana, *Can. J. Chem.*, **31**, 585 (1953).

[8] M. H. Karger and Y. Mazur, *J. Amer. Chem. Soc.*, **90**, 3878 (1968).

[9] M. H. Karger and Y. Mazur, *ibid.*, **91**, 5663 (1969).

[10] We found mixed anhydrides to be almost insoluble in hydrocarbon solvents. The best solvent for recrystallization is acetic anhydride. *Cf.* W. Flavell and N. C. Ross, *J. Chem. Soc.*, 5474 (1964).

[11] See ref 10: Flavell and Ross found that mesitylene disulfonyl chloride and silver acetate in acetic anhydride at 80° for 18 hr gave 27% mixed anhydride but after 16 hr in acetonitrile gave only a 50% yield of the anhydride.

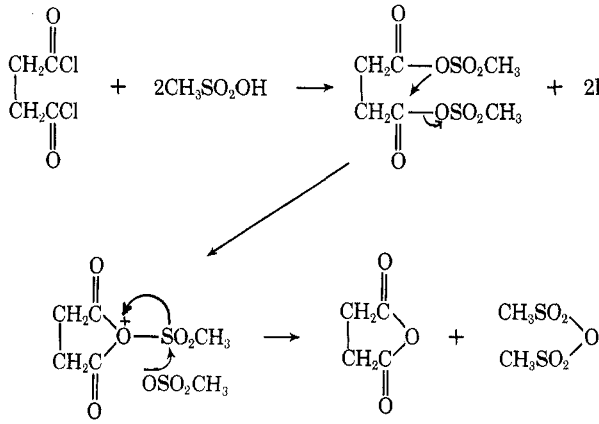
reduced, and higher temperature and more prolonged reaction times become necessary. Thus chloroacetyl chloride and methanesulfonic acid did not react completely until heated for 4 hr at 110° when almost all starting material was consumed. The reaction mixture was, however, a complex mixture of decomposition products together with less than 20% of the desired product (Table I).

Synthesis *via* Acid Anhydride.—An alternative synthetic procedure to that outlined above consists of heating an excess of carboxylic anhydride with the sulfonic acid for 20–30 min at 120° followed by removal under high vacuum of the excess anhydride together with the free acid formed in the reaction (eq 2).

$$(CH_3CO)_2O + CH_3C_6H_4SO_2OH \longrightarrow CH_3COOSO_2C_6H_4CH_3 + CH_3COOH \quad (2)$$

Acetyl *p*-toluenesulfonate and trichloroacetyl *p*-toluenesulfonate were prepared in this fashion. With higher molecular weight anhydrides, reaction in this manner is complicated by the involatility of both anhydride and acid, necessitating higher temperatures for their removal which cause decomposition of product. In general, the acid chloride method is much to be preferred from such practical considerations.

Reaction of Diacyl Chloride and Sulfonic Acids. Synthesis of Sulfonic Anhydrides.—When succinoyl chloride was reacted with sulfonic acids the expected di-mixed anhydrides were not isolated, but presumably decomposed under the reaction conditions (60°, 2 hr) to give a mixture of sulfonic anhydride and succinic anhydride. Trituration of the reaction mixture with ether effected complete separation, succinic anhydride being almost insoluble (eq 3). This reaction provided a good synthesis of sulfonic anhydrides in a clean reaction of great simplicity. Yield averaged 80%. With oxalyl chloride the sulfonic anhydride was also obtained but in low yield (Table II).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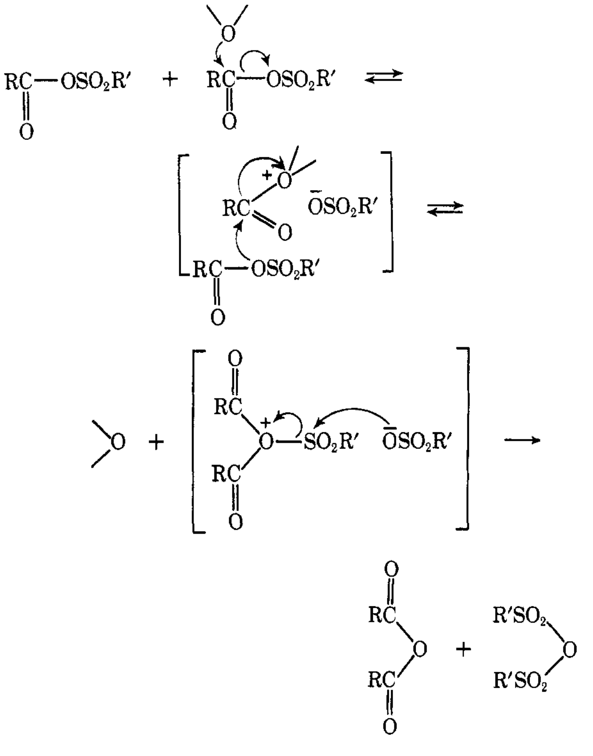
Thermal Decomposition of Mixed Sulfonic–Carboxylic Anhydrides. Below 130°.—The disproportionation of acyl sulfonates has been reported by Flavell and Ross[10] who stated that, as a preparative method for sulfonic anhydrides, thermal disproportionation was unsatisfactory due to decomposition of the sulfonic anhydrides at the temperature required for disproportionation. We have studied the thermal behavior of both mixed sulfonic–carboxylic and simple sulfonic anhydrides and wish to report that careful heating of the former provides an eminently satisfactory synthetic method by which large amounts of the latter can be prepared in excellent yield and very simple fashion.

We have found that not one but two thermal decomposition reactions are simultaneously underway when mixed sulfonic–carboxylic anhydrides (with one or more hydrogens β to the carbonyl) are heated. Below a fairly specific temperature of 130° only a simple disproportionation reaction leading to a mixture of carboxylic and sulfonic anhydrides is observed (eq 4). This reaction is

$$2CH_3COOSO_2CH_3 \longrightarrow (CH_3CO)_2O + (CH_3SO_2)_2O \quad (4)$$

a general one. The disproportionation reaction appears to be acid catalyzed. Thus, when acetyl methanesulfonate in which the acid content had been reduced to less than 0.5% by prolonged reflux in acetyl chloride was distilled at 120° (10^{-3} mm), 85% of the mixed anhydride was recovered. When, however, the acid content was increased to 5%, distillation under identical conditions gave only 10% of mixed anhydride, disproportionation having been promoted to the extent that over 50% yield of recrystallized methanesulfonic anhydride was obtained from the residue.

In solution the disproportionation was facilitated by polar solvents as has been observed previously.[10] Thus in acetonitrile we observed 25% disproportionation of acetyl methanesulfonate after 16-hr reflux, the remaining 75% being unchanged.[11] A more rapid catalytic effect is observed in oxygenated solvents; acetyl *p*-toluenesulfonic anhydride dissolved in ether does not recrystallize and the nmr spectrum of the evaporated solution shows obstinate retention of ether even after 2 hr at 10^{-3} mm. The residual oil on heating at 30° for 12 hr undergoes almost complete disproportionation. The extent of this catalysis is a consequence of coor-


(5)

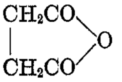
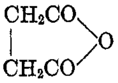
$R = CH_3$
$R' = CH_3C_6H_4$

TABLE I
PREPARATION OF MIXED SULFONIC–CARBOXYLIC ANHYDRIDES

Acid chloride[a]	Acid	Product	Registry no.	Reaction conditions (hr, °C, solvent)	Yield,[b] %	Nmr, δ (ppm)[c]
CH_3COCl (2.5)	CH_3SO_3H	$CH_3COOSO_2CH_3$	5539-53-7	16, 55	85[d]	2.28 s, 3.33 s
CH_3COCl	$C_7H_7SO_3H$	$CH_3COOSO_2C_7H_7$[e]	26908-82-7	5, 55	97 (90, 4)	2.13 s, 2.44 s, 7.64 q
C_2H_5COCl (3.0)	$C_7H_7SO_3H$	$C_2H_5COOSO_2C_7H_7$	26926-29-4	2, 70	100 (75, 2)	1.08 t, 2.45 q, 2.47 s, 7.6 m
C_2H_5COCl	CH_3SO_3H	$C_2H_5COOSO_2CH_3$	26926-30-7	4, 80	98 (80, 15)	1.20 t, 2.58 q, 3.26 s
$C_6H_5CH_2COCl$	CH_3SO_3H	$C_6H_5CH_2COOSO_2CH_3$	26926-31-8	16, 80, C_6H_6	100 (70, 5)	3.20 s, 3.73 s, 7.32 s
$C_6H_5CH_2COCl$	$C_7H_7SO_3H$	$C_6H_5CH_2COOSO_2C_7H_7$	26926-32-9	5, 80, C_6H_6	100 (65, 10)	2.42 s, 3.68 s, 7.27 s, 7.6 m
$CH_3CH_2CH_2COCl$	CH_3SO_3H	$CH_3CH_2CH_2COOSO_2CH_3$	26926-33-0	5, 80, C_6H_6	93 (70, 15)	1.00 t, 1.71_6, 2.52 t, 3.3 s
$(CH_3)_2CHCOCl$	CH_3SO_3H	$(CH_3)_2CHCOOSO_2CH_3$	26926-34-1	5, 80, C_6H_6	94 (70, 20)	1.26 d, 2.70_6, 3.32 s
C_6H_5COCl (1.0)	CH_3SO_3H	$C_6H_5COOSO_2CH_3$	26926-35-2	5, 80, C_6H_6	90 (50, 25)	3.48 s, 7.80 m
C_6H_5COCl (1.0)	$C_7H_7SO_3H$	$C_6H_5COOSO_2C_7H_7$[f]	13079-28-2	5, 80, C_6H_6	88 (60, 25)	2.42 s, 7.7 m
$ClCH_2COCl$ (1.0)	CH_3SO_3H	*g*		4, 110		8 singlets[g]

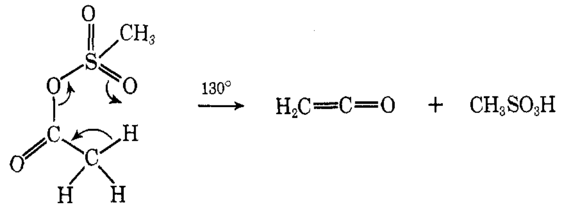
[a] Twofold molar excess used except where noted in parentheses. [b] First figure gives crude yield, second gives percentage product in crude material as estimated from the nmr spectrum, and the final figure gives the *molar* percentage of free acid estimated from the intensity of the acid proton in the nmr. [c] s = singlet, etc.; number subscript = multiplicity. [d] Distilled analytically pure, bp 70–72° (10^{-3} mm); lit. (ref 6) 56° (10^{-2} mm). [e] Mp 54–56°. [f] Mp 55–58°, ref 4. [g] The product was a mixture of six compounds: (1) CH_3SO_3H, (2) $(CH_3SO_2)_2O$, (3) $(ClCH_2CO)_2O$, (4) $ClCH_2COCl$, (5) $ClCH_2CO_2H$, (6) $ClCH_2COOSO_2CH_3$.

TABLE II
SYNTHESIS OF SULFONIC ANHYDRIDES FROM DIACYL CHLORIDES

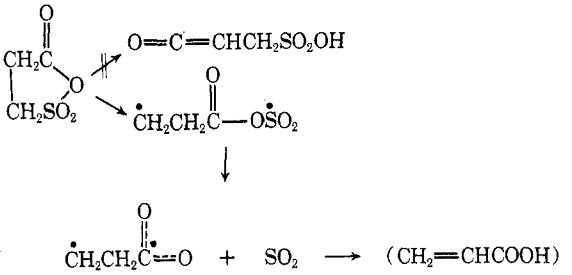
Acid chloride	Acid	Product	Reaction conditions (hr, °C, solvent)	Yield, %	Nmr, δ (ppm)
$(CH_2COCl)_2$ (0.5)	CH_3SO_3H	(1) $(CH_3SO_2)_2O$	2, 60	90	3.43 s
		(2) 		73	3.00 s
$(CH_2COCl)_2$ (0.5)	$C_7H_7SO_3H$	(1) $(C_7H_7SO_2)_2O$	2, 80, C_6H_6	73	2.45 s 7.56 q
		(2) 		100	3.00 s
$(COCl)_2$ (0.5)	CH_3SO_3H	$(CH_3SO_2)_2O$	6, 63	30	3.43 s

dination with oxygen depicted in eq 5 and observed in the facile cleavage of ethers by acyl sulfonates.[8,9]

Synthesis of Sulfonic Anhydrides by Pyrolysis of Mixed Anhydrides.—From the above observations it is clear that as long as the temperature remains below 130°, pyrolysis of mixed sulfonic–carboxylic anhydrides can provide a facile synthesis of sulfonic anhydrides. Simple heating of freshly prepared mixed anhydride on a water bath for sufficient time to ensure complete disproportionation gives almost complete conversion. The product can be recovered either by distillation or by extraction of the residue with ether, which deposits the pure anhydride on cooling, leaving any sulfonic acid formed *via* the alternative pathway (*vide infra*) in the residue. Yields are good, up to 80% on unrecovered sulfonic acid.


(6)

Thermal Decomposition of Mixed Sulfonic–Carboxylic Anhydrides. B. Above 130°.—At about 130° a second reaction predominates (for those anhydrides with transferable hydrogen β to the carbonyl group), in which the sulfonic acid is regenerated with simultaneous evolution of ketene.[12] This latter was trapped in cooled hexane and characterized by its ir frequency (2310 cm^{-1} [13]) and by its conversion on addition of ethanol to ethyl acetate (eq 6). The thermal decomposition of the cyclic anhydride of β-sulfopropionic acid[14] does not follow this course to yield the expected ring-opened sulfonic acid–ketene or a derivative. Under conditions in which acetyl sulfonates speedily decompose quantitatively to the respective sulfonic acid (2 min at 130°), β-sulfopropionic anhydride remains unchanged even after 2 hr at 130°. More vigorous heating to 180° has been observed to induce a slow decomposition to yield, ultimately, acrylic acid after extrusion of SO_2[15] (eq 7). This result would argue in favor of


(7)

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[12] The ease of ketene formation (130°) is in contrast with the temperature (500°) required for its generation from acetic anhydride. See, for example, G. J. Fisher, A. F. Mclean, and A. W. Schnizer, *J. Org. Chem.*, **18**, 1055 (1953).

[13] For which in the vapor state a strong band at 2150 cm^{-1} is observed: L. Grimke Drayton and H. W. Thompson, *J. Chem. Soc.*, 1416 (1948).

[14] M. S. Kharasch, T. H. Chao, and H. C. Brown, *J. Amer. Chem. Soc.*, **62**, 2393 (1940).

[15] T. Nagai, K. Nishitomi, and N. Togura, *Tetrahedron Lett.*, 2419 (1966).

intramolecular reaction for high-temperature thermal decomposition of mixed anhydrides since, in such a case, β-sulfopropionic anhydride would remain inert or follow an alternative reaction path as indeed is observed. On the other hand an intermolecular mechanism would favor an analogous reaction for the cyclic mixed anhydride as for the general acyclic case.

Thus reaction 6 is more likely to be intramolecular in contradistinction to reaction 4 which is most easily visualized as intermolecular.

Thermal Decomposition of Sulfonic Anhydrides.—That the above reaction of mixed anhydrides to give sulfonic acid and ketene is not merely a consequence of prior disproportionation followed by decomposition of the sulfonic anhydride to sulfonic acid was established by examining the thermal behavior of sulfonic anhydrides. Thus, methanesulfonic anhydrides decomposed only above 250° to give methanesulfonic acid (70%), residual intractable polymer (15%), and sulfene which presumably did not survive its conditions of generation (eq 8). The reaction is analogous to mixed anhydride

$$CH_3SO_2OSO_2CH_3 \xrightarrow{250^\circ} CH_3SO_3H + (CH_2{=}SO_2) \qquad (8)$$

intramolecular decomposition (eq 6). Under the terms of this reaction *p*-toluenesulfonic anhydride should not decompose in the same manner. When this anhydride was heated in a sealed evacuated tube to 230°, a black intractable polymeric solid, which gave no acid reaction on boiling with water, was the only nonvolatile product. Liquid SO_2 and toluene were collected at the mouth of the tube.

Experimental Section[16]

Mixed Sulfonic–Carboxylic Anhydrides.[17] **A. From Acid Chloride–Acetyl Methanesulfonate.**—A mixture of 96.1 g of methanesulfonic acid (1.0 mol) and 200 g of acetyl chloride (2.5 mol) was gently heated under reflux for 16 hr, moisture being carefully excluded. No further evolution of HCl gas being observed, the excess acetyl chloride was removed under vacuum at room temperature from the deep red reaction mixture. Careful distillation ($<10^{-2}$ mm, oil bath temperature below 120°) gave 117.2 g (85%) of acetyl methanesulfonate, a pale yellow oil solidifying below 0°: ir (smear) 1810 cm^{-1} (C=O); nmr δ 2.28 (s, 3, $COCH_3$) and 3.33 (s, 3, SO_2CH_3).

Anal. Calcd for $C_3H_6O_4S$: C, 26.08; H, 4.38; S, 23.21. Found: C, 26.11; H, 4.46; S, 23.18.

Acetyl *p*-Toluenesulfonate.—Anhydrous *p*-toluenesulfonic acid (92.5 g, 0.54 mol) was gently heated under reflux in 150 g of acetyl chloride (1.9 mol) until evolution of HCl had ceased (3–5 hr). The excess acetyl chloride was removed at room temperature under vacuum, leaving 112.5 g (97.5%) of crude acetyl *p*-toluenesulfonate as an off-white crystalline mass: mp 54–56°; ir ($CHCl_3$) 1820 (C=O) and 1600 cm^{-1} (aromatic C=C); nmr δ 2.13 (s, 3, $COCH_3$), 2.44 (s, 3, $C_6H_4CH_3$), and 7.64 (AB system J_{AB} = 8 Hz, Δ_{AB} = 35 Hz, 4, *p*-C_6H_4). *p*-Toluenesulfonic anhydride, present as an impurity (*ca.* 10%), was removed by cooling an ether solution of the crude product when the *p*-toluenesulfonic anhydride present was deposited from solution.

B. From Acid Anhydride–Acetyl *p*-Toluenesulfonate.—Anhydrous *p*-toluenesulfonic acid (264 g, 1.5 mol) was dissolved in an excess of 375 g of acetic anhydride (2.7 mol) and the mixture heated in an oil bath at 130° for 30 min. Excess acetic anhydride together with acetic acid formed in the reaction were removed by distillation under high vacuum at a temperature <70°. The residual oil, on cooling, solidified to 315 g (96%) of a red crystalline mass. The nmr spectrum of the product was identical with that of the sample prepared above, the proportion of free acid being about 10%, as estimated from the relative intensity of the free acid proton in the nmr.

Sulfonic Anhydrides.[18] **Methanesulfonic Anhydride. Method 1.**—A mixture of 200 g of acetyl chloride (2.5 mol) and 96.1 g of methanesulfonic acid (1.0 mol) was refluxed for 5 hr, when the proportion of free acid estimated from the nmr was 5%. The mixture was slowly distilled at a bath temperature of 120° (0.1 mm) until no more acetyl methanesulfonate came over (5–15%). The almost black pot residue was repeatedly extracted with ether; the extracts were dried, decolorized, concentrated, and cooled, depositing 45 g (52%) of methanesulfonic anhydride, mp 68°, mmp 70° (lit.[19] 69.5–70.5°), nmr δ 3.45 (s, 3, CH_3SO_2). Methanesulfonic acid (32 g, 33%) was recovered by distillation from the ether-insoluble residue, bp 140–142 (0.1 mm).

Method 2 (Table II).—A mixture of 34.4 g of succinoyl chloride (0.22 mol) and 42.3 g of methanesulfonic acid (0.44 mol) was heated at 60° for 2 hr, after which the mixture was placed under high vacuum at room temperature.[20] The residual solid was triturated with dry ether leaving 16.5 g (73%) of succinic anhydride, mp 119°, mmp 120°. The ether solution was concentrated and cooled to 0° collecting 24.3 g of methanesulfonic anhydride, mp 56–60°. Repeated concentration and cooling yielded two further crops (8.0 g, mp 62–64°; and 2.7 g, mp 66–68°). Total yield was 35.0 g (90%).

Thermal Decomposition of Acetyl Methanesulfonate. A.—A stream of dry nitrogen was passed through 6.65 g of acetyl methanesulfonate (20.7 mmol) into dry hexane cooled below −30°. The sulfonate was then heated at 130° for 15 min. The nmr spectrum of the residue showed the total absence of starting material or of material other than methanesulfonic acid. The residue (6.2 g) was dissolved in water. Extraction with ether yielded 80 mg (1.3%) of nonacidic material. The solution ir spectra of the hexane before and after heating were compared. They were not identical, an intense band at 2310 cm^{-1} being present in the latter. This band disappeared on warming the solution to room temperature and was converted, on addition of ethanol, to a band at 1720 cm^{-1}. When the experiment was repeated, passing the effluent gas into a solution of diisopropylamine in ether, evaporation of this solution to dryness left an oil, whose nmr spectrum possessed a sharp singlet at δ 2.0. When the experiment was repeated in a sealed system and heating commenced at 70°, the sulfonate remained unchanged until 128°, when it rapidly darkened and decomposed, with evolution of gas, which was complete in 2 min.

B.—A solution of acetyl methanesulfonate (10 ml) in dry acetonitrile (25 ml) was refluxed for 16 hr. The acetonitrile was removed *in vacuo*. The nmr spectrum of the residue showed it to consist of starting material (75%) and an equimolar mixture acetic and methanesulfonic anhydrides (25%). No methanesulfonic acid was detected.

C.—When acetyl *p*-toluenesulfonate was heated to 130° in a manner identical with that of the methanesulfonate (A above), the dark residue consisted solely of *p*-toluenesulfonic acid (97%).

Thermal Decomposition of Methanesulfonic Anhydride.—Methanesulfonic anhydride (4.0 g) was heated at progressively higher temperatures from 25 to 300° under a stream of nitrogen. Decomposition commenced at 250° as evidenced by evolution of gas and darkening of the hitherto clear liquid and was complete after 15 min. The black residue contained mostly methanesulfonic acid, recovered by high vacuum distillation (1.6 g, 71%). The residue, an insoluble black solid, was completely intractable (600 mg).

Thermal Decomposition of *p*-Toluenesulfonic Anhydride.—*p*-Toluenesulfonic anhydride (600 mg) was heated in a sealed, evacuated tube to 230°, when a colorless liquid distilled and collected at the mouth of the tube. After heating for a further 15 min, the tube was cooled and opened. The liquid at the mouth consisted of toluene and SO_2. The residue at the foot of the tube, a black intractable solid, gave no reaction to litmus after being boiled with water.

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[16] Melting points are uncorrected. Infrared spectra were determined with Perkin-Elmer Infracord recording spectrophotometer. The nmr spectra were determined on a Varian A-60A spectrophotometer in $CDCl_3$; peak positions are indicated in ppm downfield from TMS serving as internal reference. Mass spectra were measured with an Atlas CH-4 instrument.

[17] The preparative procedures for all mixed anhydrides described in Table I closely followed these described below. Exact conditions, where these vary, are given in Table I.

[18] The two procedures illustrated below for methanesulfonic anhydride are equally applicable to other sulfonic anhydrides, the reaction conditions and work-up procedure being identical.

[19] L. Field and P. H. Settlage, *J. Amer. Chem. Soc.*, **76**, 1222 (1954).

[20] The observed loss of weight was 16.0 g. That required for evolution of 2 mol of HCl is 16.06 g.