[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF VANDERBILT UNIVERSITY]

# Alkanesulfonic Acid Anhydrides[1]

BY LAMAR FIELD AND PAUL H. SETTLAGE

RECEIVED SEPTEMBER 28, 1953

Methanesulfonic anhydride (I) and ethanesulfonic anhydride (II), chosen as reasonably representative alkanesulfonic anhydrides, were prepared from the corresponding acids by means of phosphorus pentoxide. I and II, as well as *p*-toluenesulfonic anhydride (III), were also prepared from the corresponding sulfonyl chlorides by the use of metallic oxides. I reacts more rapidly than does methanesulfonyl chloride (IV) in sulfone formation with benzene, and forms methanesulfonyl isocyanate in much better yield (38%) than does IV (5%). Results with I and IV are seemingly similar in the sulfonylation of diethyl malonate. I resembles trifluoroacetic anhydride in promoting esterification of acetic and benzoic acids. Other reactions of I are also discussed, including those with pyridine and phenylmagnesium bromide.

A previous communication[2] from this Laboratory described the conversion of representative aromatic sulfonic acids to the corresponding anhydrides by means of phosphorus pentoxide, and dealt with several aspects of the chemistry of these anhydrides.[3] The present paper reports an extension of these studies, particularly with reference to alkanesulfonic acid anhydrides.

Methanesulfonic anhydride (I) and ethanesulfonic anhydride (II) were prepared in the manner reported[2] for benzenesulfonic and *p*-toluenesulfonic anhydride (III), but under milder conditions. Treatment of methanesulfonic acid with acetic anhydride or isopropenyl acetate[6] did not yield I, suggesting that the bond-strength relations involved in formation of I are unfavorable in these instances.

Alkanesulfonic anhydrides, as exemplified by I and II, are seemingly best purified by distillation, and subsequent recrystallization when feasible. III, however, decomposes partially during distillation, so that recrystallization alone is preferable. The identity of I was established by mixture m.p. with authentic material,[7] and was confirmed for both I and II by conventional methods.

Sulfonyl chlorides are frequently more easily accessible than the sulfonic acids. A direct synthesis of anhydrides from the chlorides accordingly appeared to deserve investigation. Carboxylic anhydrides may be obtained from acyl chlorides by reaction with pyridine and, subsequently, with water.[8] Exploratory attempts to obtain I from methanesulfonyl chloride (IV) in this way were not encouraging. Likewise, attempted extension to IV of a conversion of benzenesulfonyl chloride to the anhydride by means of oxalic acid[9] did not afford promising results. McGookin and Page[10] recently described the preparation of carboxylic anhydrides from acyl halides and metallic oxides. In a modification of this procedure, IV and mercuric oxide gave I in 82% yield. Silver oxide gave similar results, but lead monoxide was virtually ineffective. Ethanesulfonyl chloride and mercuric oxide gave II in 76% yield, and *p*-toluenesulfonyl chloride gave III in 69% yield, thus suggesting a probable generality for this method.

The previously discussed[2] rather broad melting range of III was studied further. Ionization can now be excluded as a significant factor in the marked depression effected in the m.p. of III by *p*-toluenesulfonic acid, since the molal freezing point depression constant ($K_f$) with this acid as solute is about 10, whereas about 20 would be expected if complete ionization occurred. The capillary softening point of III was found to decrease about 40° in the presence of only 1.7% of the acid.

I resembles III in melting-point characteristics, although the breadth of the range is much less marked. In this instance also, significant ionization of sulfonic acid impurity seems unlikely, since the $K_f$ of I is about 14 with both methanesulfonic acid and 2,4-dinitrotoluene. The less broad melting ranges observed with I seem most reasonably ascribable to the smaller differential existing between the melting points of I and methanesulfonic acid (m.p.[11] 20°), in comparison with that existing between the melting points of III and *p*-toluenesulfonic acid.

The lack of success noted above in obtaining I from IV with pyridine and water suggested that I might indeed have been formed, but rendered inaccessible to isolation through formation of a pyridine complex. Subsequently, the formation of a stable solid 1:1 molecular complex was noted with III and pyridine.[2] A similar pyridine complex has now been observed for I. It hydrolyzes rapidly in water; characterization was effected by subsequent quantitative neutralization. A convenient and efficient means of removing sulfonic anhydrides from reaction mixtures is provided by treatment with pyridine and subsequent washing with dilute aque-

---

[1] Abstracted mainly from the Ph.D. thesis of Paul H. Settlage, September, 1953.

[2] L. Field, THIS JOURNAL, **74**, 394 (1952).

[3] A noteworthy addition to previously summarized[2] preparations of sulfonic anhydrides has been contributed recently by Khorana,[4] who obtained anhydrides from sulfonic acids by using substituted carbodiimides (RN = C = NR). This apparently general reaction seems especially promising for use with valuable sulfonic acids, where the use of a less direct and more expensive route is expedient. The preparation of aromatic sulfonic anhydrides from the acids by the use of thionyl chloride is well known (see ref. 2 for citations). In contrast, methanesulfonic acid has seemingly given only the chloride. It is accordingly noteworthy that in one instance our use of thionyl chloride in a well-established procedure[5] gave the chloride in only about 23% yield, but the anhydride in 67% yield (m.p. 60.5–64°). NOTE ADDED IN PROOF: L. N. Owen and S. P. Whitelaw [*J. Chem. Soc.*, 3723 (1953)] recently have reported that methanesulfonic anhydride may be prepared in 82% yield by heating the acid with thionyl chloride. These authors also pointed out that use of the anhydride, rather than the chloride, may be advantageous in the preparation of certain types of methanesulfonates, in agreement with our conclusion that the anhydride may be preferable in special instances.

[4] H. G. Khorana, *Can. J. Chem.*, **31**, 585 (1953).

[5] C. R. Noller and P. J. Hearst, THIS JOURNAL, **70**, 3955 (1948); *Org. Syntheses*, **30**, 58 (1950).

[6] Kindly provided by Tennessee Eastman Corp., Kingsport, Tenn.

[7] O. C. Billeter, *Ber.*, **38**, 2015 (1905).

[8] H. Adkins and Q. E. Thompson, THIS JOURNAL, **71**, 2242 (1949).

[9] R. G. Shepherd, *J. Org. Chem.*, **12**, 275 (1947).

[10] A. McGookin and H. Page, *J. Chem. Soc.*, 2769 (1951).

[11] A. Berthoud, *Helv. Chim. Acta*, **12**, 863 (1929).

ous sodium bicarbonate. The complex also reacts readily with phenol to form phenyl methanesulfonate in 85% yield, a reaction useful for both characterization and preparation.

Bourne and co-workers[12] have recently reported a mild preparation of carboxylic esters through direct reaction of the acid with hydroxy compounds in the presence of trifluoroacetic anhydride. Since methanesulfonic acid resembles trifluoroacetic acid in its strongly acidic character, it seemed of interest to determine whether or not I might also serve for esterification reactions. This proved to be feasible; β-naphthol was acetylated and ethylene glycol dibenzoylated, both conditions and results being similar to those applying for the fluoro anhydride. Sucrose, however, could not be satisfactorily converted to the octaacetate.

In the Friedel–Crafts synthesis of sulfones, benzenesulfonic anhydride gives results superior to those obtained with the sulfonyl chloride.[2] I likewise reacts readily with benzene in the presence of aluminum chloride, and gives methyl phenyl sulfone (V) in 77% yield. Repetition of this experiment with the substitution of the sulfonyl chloride IV for I gave V in only 2% yield (the fact that the amount of catalyst used with I is in large excess with IV may have contributed, however, to this low yield).[13] IV, on the other hand, does give V in 77% yield when steam-bath heat is applied for 15 hours.[13] Evidently, in this reaction, I reacts considerably more rapidly than does IV. The sufficiency of mild conditions for the reaction of I suggests that anhydrides may be useful in instances where sensitive substances are involved.

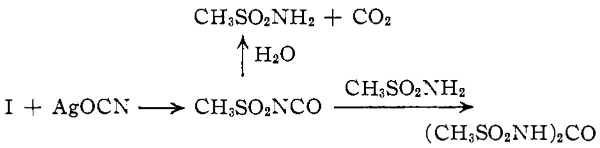
Sulfones also have been prepared directly by the reaction of aromatic sulfonic acids, aromatic hydrocarbons, and phosphorus pentoxide[14]; the anhydride is almost certainly an intermediate. Attempts were made to realize the complete utilization of methanesulfonic acid for the synthesis of V by reconversion of by-product sulfonic acid to anhydride, the desired result being summarized by the equation

$$3C_6H_6 + P_2O_5 + 3CH_3SO_3H \longrightarrow 3CH_3SO_2C_6H_5 + 2H_3PO_4$$

The crude V obtained using boiling benzene in this way amounted to 42%, although only 27% of reasonably pure V was isolated. Use of hydrocarbons of higher boiling point and more efficient mixing might well result in much improved yields.

The reaction of I with diethyl ethoxymagnesiomalonate gave diethyl methylsulfonylmalonate in 56% yield. This result closely resembles that obtained in the reaction of IV and diethyl sodiomalonate.[15] The reaction of I with diethyl sodiomalonate, however, gave the sulfonylmalonate in only 25–34% yield. In the characterization of the sulfonylmalonate by acid hydrolysis, methylsulfonylacetic acid could not be crystallized and was converted to dimethyl sulfone.

Billeter reported that the reaction of methanesulfonyl chloride and silver cyanate gives methanesulfonyl isocyanate in 5% yield.[16] Since I was also isolated in this reaction, possibly its presence may actually have been responsible for the isocyanate isolated; in this event, pure I should serve with greater effectiveness than IV. When this proposition was tested, methanesulfonyl isocyanate was formed from I in 38% yield; it was characterized by its very facile hydrolysis which led to carbon dioxide and methanesulfonamide (100% yield), and by conversion to 1,3-bis-(methanesulfonyl)-urea. Potassium cyanate was ineffective.



$$\begin{tikzcd} & CH_3SO_2NH_2 + CO_2 & \\ I + AgOCN \arrow[r] & CH_3SO_2NCO \arrow[u, "H_2O"'] \arrow[r, "CH_3SO_2NH_2"] & (CH_3SO_2NH)_2CO \end{tikzcd}$$

The reaction of I with phenylmagnesium bromide resembles that of benzenesulfonic anhydride[2] in complexity. V was isolated in 8% yield, together with small amounts of biphenyl and phenol.

Several other seemingly attractive possibilities for I were investigated with unpromising results. These included attempted Perkin-type condensation of I with benzaldehyde in the presence of potassium carbonate, tri-*n*-butylamine, sodium metal and potassium acetate; also a Dakin–West[17] type reaction between I and N-acetylphenylalanine with pyridine in toluene or with potassium acetate in N-dimethylformamide. The likelihood nevertheless exists that these condensations could be effected in the presence of a sufficiently strong base which will not cleave the I. III with the sodium or silver salts of *p*-toluenesulfinic acid in a variety of solvents gave di-*p*-tolyl disulfone in a maximum yield of only 6%.

**Acknowledgment.**—This investigation was supported by funds provided by the Office of Ordnance Research, U. S. Army. The authors are indebted also both to Research Corporation of New York, and to the Carnegie Foundation and Vanderbilt University jointly for generous grants during the earlier phases.

## Experimental[18]

**Preparation of Anhydrides from the Acid with Phosphorus Pentoxide.** (a) **Methanesulfonic Anhydride (I).**—The procedure used is a modification of a previous one.[2] One-half of a mixture of 300 g. of phosphorus pentoxide and 90 g. of Super-cel was added with manual stirring to 305 g. of 95% methanesulfonic acid[19] and 10 g. of Gooch asbestos in a flask provided with a calcium chloride tube. When reaction had largely subsided, the mixture was heated at 80° for 2.5 hours while the remainder of the mixture was added in five portions and mixed in as well as possible. Heating was continued for three hours, and the I then extracted[2] with a total of 1500 ml. of ethylene chloride.[20] Removal of solvent and distillation gave 193 g. of slightly oily I, b.p. 105–109° (1 mm.). Recrystallization[2] of the distillate using

---

[12] E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).

[13] W. E. Truce and C. W. Vriesen, THIS JOURNAL, **75**, 5032 (1953). We are indebted to Dr. Truce for information prior to its publication.

[14] A. Michael and A. Adair, *Ber.*, **10**, 583 (1877); **11**, 116 (1878).

[15] H. Böhme and R. Marx, *ibid.*, **74B**, 1664 (1941) [*C. A.*, **37**, 79 (1943)].

[16] O. C. Billeter, *ibid.*, **38**, 2013 (1905).

[17] Leading references on this reaction are given by J. A. King and F. H. McMillan, THIS JOURNAL, **73**, 4451 (1951).

[18] See footnotes 16, 17 of ref. 2. Solvent removal was effected under the reduced pressure provided by an aspirator which was connected, when necessary, through a calcium chloride tube.

[19] Kindly provided by the Indoil Chemical Co., 910 S. Michigan Ave., Chicago, Ill.

[20] Washed with sulfuric acid, dried over phosphorus pentoxide, and distilled; b.p. 83.1–83.3°.

1200 ml. of dry ether–benzene[2] (2:1) gave 143 g. (55%) of nearly colorless I, m.p. 65.5–67°; an additional 3% of I, m.p. 66–67.5°, was obtained by recrystallization of material from the mother liquor. Further recrystallization of similarly prepared I gave colorless crystals having a constant m.p. of 69.5–70° which did not depress the m.p. of authentic[21] I; hydrolysis equiv. 87 (calcd. for I, 87); methanesulfonamide, m.p. and mixture m.p. 89.5–91°.

In experiments dealing with the preparation of I, use of only 10 g. of Super-cel and 5 g. of asbestos resulted in very oily product (67% yield); direct distillation of 20 g. of acid with 9.4 g. of phosphorus pentoxide gave a partly liquid product, although this upon washing with cold ether gave I in 55% yield, m.p. 61–64°; substitution (in the original preparation of I) of a cold petroleum ether–ether wash for the distillation step prior to recrystallization lowered the yield to 38%; an attempt to remove impurities from an ethylene chloride solution of crude I by rapid washing with ice-water resulted in loss of 82% of the I.

The freezing point of I which had been recrystallized to constant m.p. was determined by the cooling curve method, with precautions for exclusion of moisture; the highest f.p. observed was 68.3°. The molal freezing point depression constant[22] ($K_f$) of I was determined with several solutes in amounts of 1–2% of the I used; the f.p. determination with each solute was repeated until unchanged values resulted in successive trials. With V, the $K_f$ was 11.4 and 10.6; with 2,4-dinitrotoluene, the $K_f$ was 14.0 and 13.7; and, with methanesulfonic acid (formed *in situ* by addition of water), the $K_f$ was 14.0. The effect of small amounts of impurity on the capillary m.p. of I was directly demonstrated by a determination made with one of the above samples of I containing 1.3% of V; the m.p. decreased from the value of 69.5–70° (softening, 69°), observed with the pure sample, to 63–66.5° (softening, 61°).

I is relatively stable to heat, 94% being recoverable after nearly 3 hours of heating at 180°; the m.p. dropped from 64–68° to 57.5–61.5°, however, and a little sulfur dioxide was evolved.

(b) **Ethanesulfonic Anhydride** (II).[23]—The procedure was similar to that used for I. The mixture of 232 g. of 95% ethanesulfonic acid, 142 g. of phosphorus pentoxide, 50 g. of Super-cel and 10 g. of asbestos, was heated, however, at 80–85° for 4 hours after addition was complete. The crude II obtained by removal of ethylene chloride followed by distillation using a modified claisen flask with a 20-cm. column yielded 125.3 g. (62%) of II, b.p. 108–116° (1.4–2 mm.). Redistillation gave II having b.p. 94° (0.5 mm.), m.p. 18–20°, $n^{25}D$ 1.4482, hydrolysis equiv. 102 (calcd. for II, 101).

*Anal.* Calcd. for $C_4H_{10}O_5S_2$: S, 31.71. Found: S, 32.38, 32.42.

II was further characterized by conversion to ethanesulfonamide, m.p. and mixture m.p. 58.5–60°.

**Preparation of Anhydrides from the Sulfonyl Chloride with Mercuric Oxide. (a) Methanesulfonic Anhydride** (I).—A mixture of 26.0 g. of yellow mercuric oxide, 22.9 g. of methanesulfonyl chloride (IV) and 25 ml. of *sym*-tetrachloroethane[24] was stirred with exclusion of moisture at the reflux temperature (146°) until all odor of sulfonyl chloride disappeared and the suspension became gray-brown (1.5 hours), and then for 10 minutes more. The supernatant liquid was decanted, and the residue washed with two 20-ml. portions of boiling ethylene chloride.[20] The solutions were centrifuged to remove a small amount of suspended solid. Removal of solvent and distillation of the residue gave 14.3 g. (82%) of white I, b.p. 92–95° (0.7 mm.), m.p. 63.5–66°. Recrystallization[2] from ether-benzene (4:1) then gave I in 67% yield, m.p. 67–68.5°, which after further recrystallization had constant m.p. 69.5–70.5° and did not depress the m.p. of I prepared using phosphorus pentoxide; hydrolysis equiv., 88.

Characterization as the sulfonamide of the I prepared in this way was best effected by means of a procedure based on one useful with the chloride.[25] Dry ammonia was passed for 2 hours into a solution of 7.18 g. of I in 40 ml. of benzene, initially with cooling, at 30–40°. The resulting solid was washed with boiling butanone, which was then combined with the benzene filtrate. Removal of solvent and recrystallization gave 2.06 g., m.p. and mixture m.p. 91–92°; a second crop, m.p. 85–89°, brought the yield to 68%.

A fivefold increase in the scale of the mercuric oxide preparation resulted in distillate (82% yield) with m.p. 65.5–68°; material of approximately this purity was used in most experiments. Results with other oxides and conditions are summarized in Table I.

TABLE I

| Oxide | Solvent (reacn. temp., °C.) | Hours of heating | Product Yield, % | Product M.p., °C. |
|---|---|---|---|---|
| $Ag_2O$ | $C_6H_5NO_2$ (90) | 7 | 70 | 58–61 |
| HgO (yellow) | $ClCH_2CH_2Cl$[20] (83) | 60 | 43 | 66–67 |
| $Ag_2O$ | $ClCH_2CH_2Cl$[20] (83) | 60 | 55 | 59–61 |
| PbO | $ClCH_2CH_2Cl$[20] (83) | 60 | Trace | 67–68 |
| PbO | $Cl_2CHCHCl_2$[24] (146) | 10 | 10 | 64–66 |

(b) **Ethanesulfonic Anhydride** (II).[23]—The procedure described for I was used with 38.6 g. of ethanesulfonyl chloride and 39.0 g. of yellow mercuric oxide except that the heating period was 2.5 hours. Distillation gave 22.9 g. (76%) of colorless II, b.p. 111–112° (2 mm.). After removal of a trace of solid impurity by centrifugation, the hydrolysis equiv. was 102; $n^{25}D$ 1.4489.

(c) ***p*-Toluenesulfonic Anhydride** (III).—The procedure described for I was followed with 13.0 g. of yellow mercuric oxide and 19.1 g. of *p*-toluenesulfonyl chloride. Distillation of the III obtained by removal of solvent was accompanied by considerable decomposition, and the distillate was quite oily. Recrystallization[2] from 1:1 ether-benzene, on the other hand, gave III in 69% yield, m.p. 123–127° (softening 105°); further recrystallization gave III (48% yield) having m.p. 128–129.5° (softening 126°) which did not depress the m.p. of authentic[2] III; hydrolysis equiv., 162 (calcd. for III, 163).

When the scale of preparation was increased fivefold, and solvents were used which had been dried only by distillation or (ether, benzene) over sodium, a typical yield after one recrystallization was 47%, m.p. 95–114° (softening, 85°); on one occasion much better results were obtained, but could not be duplicated.

III recrystallized to constant m.p. had a f.p. (cooling-curve method) of 129.6°, 129.9°; these values are probably more nearly correct than the value of 128.5° previously reported.[2] The $K_f$, determined as described for I, with *p*-toluenesulfonic acid (formed *in situ* by addition of water) as a solute was 9.3 and 10.4.

The presumed[2] effect of small amounts of *p*-toluenesulfonic acid on the capillary m.p. of III was substantiated in a direct way by addition of sufficient water to III to give an acid content of 1.7%. The capillary m.p. then dropped from 128–130° (softening 124°) to 106–118° (softening 83°); traces of moisture introduced, despite precautions, in loading the capillary may, however, figure in this decrease to some extent.

**Reaction of I with Pyridine.**—Pyridine[26] (2.00 g.) was added to 4.40 g. of I (m.p. 65–67°) in 75 ml. of dry benzene at 15°; a white precipitate began to form immediately. The crystalline mass resulting after 3 days at 25° was cooled, and as much benzene as possible was removed through a filter stick under pressure of dry nitrogen. The residue was then dried at 3 mm. pressure. There was obtained 6.33 g. (99%, assuming a 1:1 complex of I and pyridine) of white powder, m.p. 92–135° dec. The solid dissolves rapidly in water; hydrolysis equiv., 125 (calcd. for 1:1 complex, 126).

For characterization, a mixture of 1.71 g. of phenol and 4.58 g. of the complex in dry benzene was allowed to stand overnight, and was then heated under reflux for 2 hr. The mixture was cooled, washed with water, and dried over

---

(21) M.p. 67.5–68°; from silver methanesulfonate and IV by the procedure of Billeter[7]; yield after partial purification, 44%, m.p. 68–70°.

(22) Calcd. according to S. Glasstone, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 646.

(23) II has been reported by W. A. Proell, C. E. Adams and B. H. Shoemaker, *Ind. Eng. Chem.*, **40**, 1129 (1948); W. A. Proell, U. S. Patent 2,489,316 (1949) [*C. A.*, **44**, 1527 (1950)]. No physical constants were given.

(24) Redistilled, b.p. 145–146.5°.

(25) L. Field and F. A. Grunwald, THIS JOURNAL, **75**, 934 (1953).

(26) Distilled from barium oxide and stored over potassium hydroxide.

anhydrous magnesium sulfate. Removal of solvent left 2.65 g. (85%) of phenyl methanesulfonate, m.p. 54–57°. Precipitation from methanol by water gave the ester with m.p. and mixture[27] m.p. 59–60.5°.

In studying removal of I from reaction mixtures, 2.4 g. of pyridine was added to 3.5 g. of I in 110 ml. of benzene. After 30 minutes, the solution was washed with aqueous sodium bicarbonate and water. Removal of solvent left only 0.01 g. of residue. A similar experiment with III (6.53 g.) and pyridine (2.4 g.) resulted in 0.1 g. of residue.

**Use of I in Esterification of Carboxylic Acids. (a) β-Naphthyl Acetate.**—I (11.0 g.) in 42 ml. of glacial acetic acid was heated at 60° for one hour and then cooled. β-Naphthol (6.00 g.) was added, and the mixture was allowed to stand for 3 days before being poured into aqueous sodium bicarbonate. A chloroform extract was washed with water and dried. Removal of solvent left 7.76 g. (100%) of tan β-naphthyl acetate, m.p. 65–67.5°, which after recrystallization amounted to 6.56 g. (85%), m.p. and mixture[28] m.p. 68.5–69°. A period of standing of 36 hours reduced the yield to 91%; when the standing period was omitted, and the mixture heated at 60° for 15 minutes the yield was 99%, m.p. 66.5–68°; use of a four-hour heating period gave a somewhat less pure product.

**(b) Ethylene Dibenzoate.**—A mixture of 7.63 g. of benzoic acid and 10.9 g. of I was heated at 85° for one hour with occasional stirring. Ethylene glycol (1.55 g.) was added, and the mixture heated for 30 minutes more, cooled, and added to aqueous sodium carbonate. Several water washes of a chloroform extract were acidic, probably because of excess I hydrolysis; after addition of pyridine, washes were neutral. Removal of solvent from the dried extract gave 5.98 g. (88%) of oily solid which after recrystallizations yielded 3.21 g. (48%) of ethylene dibenzoate, m.p. and mixture[29] m.p. 71.5–72.5°. A heating period of 1.5 hours gave less pure product.

**Friedel–Crafts Type Reaction of I.**—The reaction of 8.75 g. of I and benzene was effected with 13.8 g. of anhydrous aluminum chloride essentially as described[2] for the preparation of diphenyl sulfone. Removal of benzene left 6.0 g. (77%) of methyl phenyl sulfone (V), m.p. 81–87°, which after trituration at 0° with 3:1 petroleum ether–ether and recrystallization from carbon tetrachloride amounted to 5.64 g. (72%), m.p. and mixture[30] m.p. 87–88°.

For the comparison of the sulfonyl chloride IV with I, the above experiment was essentially repeated except that an equimolar amount of IV replaced the I. Removal of the benzene left 0.47 g. (6%) of very oily V, which after recrystallization from aqueous ethanol amounted to 0.12 g. (2%), m.p. 84–86°; further recrystallization gave V of m.p. and mixture m.p. 85–87°.

A significant indication of the reactivity of I is provided by an experiment similar to that above, but with omission of the reflux period; V was obtained in 71% yield, m.p. 86–87°. In an attempt to utilize methanesulfonic acid directly by converting original and by-product acid to I, a mixture of 15.2 g. of methanesulfonic acid,[19] 0.5 g. of asbestos, 15 g. of phosphorus pentoxide and 5 g. of Super-cel was stirred well manually and, after 15 minutes when reaction had subsided, was heated for 3 hours at 85°. Dry benzene (50 ml.) was then added, and the mixture was stirred mechanically, with occasional manual loosening, and heated under reflux for 6 hours. One hour after addition of the benzene, 5 g. of phosphorus pentoxide and 1.5 g. of Super-cel was added; this addition was repeated after 5 hours more and 1.5 ml. of 85% phosphoric acid was also added. After an additional reflux period of 12 hours, during which stirring could not be continued, 1:3 ethanol-water was added to destroy any residual I, and benzene was removed by distillation. The aqueous ethanol solution and an extract of the reaction residue were filtered and upon cooling deposited 9.76 g. (42%[31]) of crude V, m.p. *ca.* 74–80°. Recrystallization gave 6.42 g. (27%[31]) of V, m.p. and mixture[30] m.p. 84–86.5°. A similar experiment, in which the materials were simply heated in benzene at 80° for 2 days, resulted in only 10%[31] of crude V, m.p. 67–78°.

**Malonic Ester Type Synthesis with I. Diethyl Methylsulfonylmalonate.**—Diethyl ethoxymagnesiomalonate was prepared by the Lund procedure essentially as previously described.[2] After addition of 9.61 g. of diethyl malonate in 10 ml. of ethanol to 1.46 g. of magnesium and 0.1 ml. of carbon tetrachloride, followed by heating under reflux for 3 hours, however, ethanol was removed under reduced pressure; 90 ml. of benzene was then added and removed, finally under reduced pressure, until a semi-solid mass remained. A solution of 8.71 g. of I in 60 ml. of dry benzene was then added during 2.5 hours at 25°, after which the mixture was stirred for 36 hours at 30° and poured into water. After addition of 25 ml. of 3 *N* hydrochloric acid and isolation[2] of the product, 6.61 g. (56%) of colorless diethyl methylsulfonylmalonate was obtained; $n^{25}\mathrm{D}$ 1.4462.

Similarly prepared material after two distillations had b.p. 143–146° (3 mm.), $n^{25}\mathrm{D}$ 1.4531, $d^{25}_{4}$ 1.2437, m.p. 23–25[32]; $M\mathrm{D}$ calcd.[33] 51.06, found 51.78 (exaltation 0.72); neut. equiv. 248 (calcd. 238).

*Anal.* Calcd. for $C_8H_{14}O_6S$: C, 40.33; H, 5.92. Found: C, 40.31; H, 5.93.

An appreciably lower yield resulted when the mixture was heated under reflux after addition of I. On the other hand, addition of I at 5° (3.5 hours) followed by stirring at 5° (2 hours) and then at 30° (15 hours) gave a result nearly identical with that above.

The presumed diethyl methylsulfonylmalonate was characterized by heating 4.04 g. with 25 ml. of 25% sulfuric acid under reflux for 18 hours (considerable carbon dioxide was evolved). Continuous extraction with chloroform and removal of solvent after drying gave 1.72 g. of oil which could not be crystallized. The oil was heated at 290° for 2 hours; distillation at 360–390° then yielded dimethyl sulfone (21% from the ester), m.p. 105–107.5°, undepressed by authentic material.[34]

**Methanesulfonyl Isocyanate.**—Silver cyanate[35] (11.67 g.) was quickly stirred into 7.83 g. of I at 100°. The temperature of a surrounding Wood metal bath was then increased to 175° in 3 minutes, whereupon a vigorous reaction ensued. After the mixture had been heated at 185° for 10 minutes, the temperature was reduced to 135° and the pressure to 2 mm. Rapid distillation then occurred, yielding 2.05 g. (38%) of methanesulfonyl isocyanate, b.p. 55° (2 mm.). Redistillation of similarly prepared material gave pure isocyanate, b.p. 38–39° (1.5 mm.), m.p. 29.5–31°, m.p. reported[16] 31°.

*Anal.* Calcd. for $C_2H_3O_3NS$: S, 26.48. Found: S, 26.39.

Hydrolysis of 0.20 g. of the product occurred with great ease with the liberation of considerable carbon dioxide and the formation of 0.16 g. (100%) of methanesulfonamide, m.p. 86.5–89°, which after recrystallization had m.p. and mixture[25] m.p. 89.5–91°.

1,3-Bis-(methanesulfonyl)-urea was prepared by a procedure based on that of Billeter[36] for 1,3-bis-(benzenesulfonyl)-urea. A mixture of 0.30 g. of methanesulfonyl isocyanate and 0.24 g. of finely ground methanesulfonamide[26] was heated at 50–65° during 20 minutes. The white product (0.54 g., 100%, m.p. 201.5–205.5°) after recrystallization from methanol had m.p. 206–209° and did not depress the m.p. of authentic[25] 1,3-bis-(methanesulfonyl)-urea.

NASHVILLE 5, TENNESSEE

---

(27) B. Helferich and P. Papalambrou, *Ann.*, **551**, 235 (1942).

(28) F. D. Chattaway, *J. Chem. Soc.*, 2495 (1931).

(29) H. C. Heim and C. F. Poe, *J. Org. Chem.*, **9**, 299 (1944).

(30) L. Field, THIS JOURNAL, **74**, 3919 (1952).

(31) The theoretical yield is based on the assumption embodied in the equation (see Discussion) that the methanesulfonic acid reacts completely with benzene.

(32) Reported[15] m.p. 30°, b.p. 175° (12 mm.).

(33) The $M\mathrm{He}$ value of 8.61 for $-SO_2-$ in sulfones was used [W. Strecker and R. Spitaler, *Ber.*, **59B**, 1757 (1926)].

(34) L. Field and John W. McFarland, THIS JOURNAL, **75**, 5582 (1953).

(35) From the mixture of aqueous solutions of silver nitrate (13.6 g.) and potassium cyanate (6.8 g.); the precipitate was washed well with water and dried to constant weight under reduced pressure over phosphorus pentoxide.

(36) O. C. Billeter, *Ber.*, **37**, 695 (1904).