hours, while the ice-bath was allowed to come slowly to room temperature. The reaction mixture was poured into a solution of sodium acetate (two moles per mole of anhydride), refluxed for 30 minutes to one hour (until the boron fluoride complexes were hydrolyzed), chilled and extracted with ether or ligroin (b.p. 30–60°).[15] When the product was soluble in the hydrolysis mixture, the solution was partly neutralized with solid sodium bicarbonate before extraction. The extracts were washed free of acid with saturated sodium bicarbonate solution and dried over Drierite. The β-diketones were isolated by distillation.

In experiments in which the reaction mixtures became difficult to stir because of the formation of solid boron fluoride complexes, ethylene chloride was used as solvent. After the reaction mixture was treated with the sodium acetate solution, the ethylene chloride was removed by distillation until the vapor temperature rose above 90°. The residue was then refluxed and worked up as described above.

(B) **Inverse Addition Procedure.**—Acetic acid[16] (0.8 mole) or ethyl acetate (0.6 mole) was placed in a three-necked flask fitted with an efficient, sealed stirrer, a gas inlet tube and an outlet tube loosely closed with a cotton plug. The flask was immersed in an ice-bath and, with vigorous stirring, boron fluoride passed in as rapidly as it was absorbed. Addition was continued (at a reduced rate as saturation was approached) until the contents of the flask became a powdery solid.[17] At this point, the acid had absorbed 75–85 mole per cent. of the reagent,[18] and the ester, 100 mole per cent. A dropping funnel was then substituted for the gas inlet tube, and a mixture of the ketone (0.2 mole) and anhydride (0.4 mole) was added with ice-bath cooling and vigorous stirring during 2–4 minutes. After stirring 30 minutes the ice-bath was removed. The reaction mixture was allowed to stand 4 hours and then worked up as described in the rapid saturation procedure. Ethyl acetate was removed in the manner described for ethylene chloride.

Alkaline Cleavage of 2-Acyl Cyclic Ketones.—The β-diketone (0.1–0.2 mole) was dissolved in excess of 5% sodium hydroxide solution (containing a molecular equivalent plus 10% of the base) and the resulting solution refluxed two hours. After washing with ether, the cooled alkaline solution was acidified with hydrochloric acid, and the liberated keto acid isolated by distillation.

2-*n*-Butyrylcyclopentanone gave a 78–90% yield of δ-*n*-butyryl-*n*-valeric acid, b.p. 140–142 at 1 mm., m.p. 38–39°, neut. equiv. calcd. 172.2, found 171.1.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.78; H, 9.37. Found: C, 62.96; H, 9.45.

2-*n*-Butyrylcyclohexanone gave a 65% yield of ε-*n*-butyryl-*n*-caproic acid, b.p. 157–158° at 2.5 mm., m.p. 42–43°, neut. equiv. calcd. 186.2, found 185.1.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.50; H, 9.74. Found: C, 64.61; H, 9.79.

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[15] Ligroin is usually advantageous, especially in acetylations, because it removes very little acetic acid from the aqueous phase, whereas ether removes a considerable amount of the acid, the subsequent removal of which requires numerous washings with sodium bicarbonate solution.

[16] For acylations with anhydrides higher than acetic anhydride, the corresponding higher carboxylic acid may be used in a similar manner.

[17] Ethylene chloride (75–100 ml.) may be used to keep the solid complex from caking, which occurred when the stirring was not sufficiently rapid.

[18] The solid appears to consist of a mixture of mono- and diacetic acid–boron fluoride complexes. The mono-acetic acid complex may be prepared conveniently on a relatively large scale and used as required, 0.6 mole being employed with 0.2 mole of ketone and 0.4 mole of anhydride. Since the diacid complex, which is a liquid (Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934)), is soluble in ethylene chloride, the solid monoacetic acid complex is obtained by saturating an ethylene chloride solution of acetic acid with boron fluoride, filtering and washing the precipitate with the solvent. It is hygroscopic and should be protected from moisture.

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Friedel–Crafts Reactions of Methanesulfonyl Chloride with Benzene and Certain Substituted Benzenes[1]

BY WILLIAM E. TRUCE AND CALVIN W. VRIESEN[2]

RECEIVED MAY 20, 1953

The Friedel–Crafts reaction of methanesulfonyl chloride with benzene has been examined with respect to the type of catalyst, time of reaction, amount of catalyst, and the effect of solvent. The reaction with toluene in the presence of aluminum chloride resulted in a mixture of isomers, the para/meta ratio indicating that the reagent exhibits comparatively low selectivity. A good yield of the *p*-isomer was obtained when chlorobenzene was treated with this reagent. Mesityl methyl sulfone was produced in a low conversion in the presence of stannic chloride. Phenyl methanesulfonate was formed in the reaction with anisole. The difference in behavior of methanesulfonyl chloride and aromatic sulfonyl chlorides in the Friedel–Crafts reaction is discussed.

Good conversions have frequently been obtained with aromatic sulfonyl chlorides in the preparation of diaryl sulfones by the Friedel–Crafts method.[3]

An early attempt[4] to apply this reaction to aliphatic sulfonyl chlorides, consisting of treating toluene with phenylmethanesulfonyl chloride in the presence of aluminum chloride, resulted in tar formation only. Methanesulfonyl chloride is reported[5] to react with benzene in the presence of excess aluminum chloride to give methyl phenyl sulfone in a conversion which is "not large." This observation was made in connection with a study of the complex of methanesulfonyl chloride with aluminum chloride; this complex decomposed to sulfur dioxide and methyl chloride when it was heated gently. Burton and Hoggarth[6] studied the reaction of methanesulfonyl chloride with hydroquinone dimethyl ether in the presence of zinc chloride and obtained *p*-anisyl methanesulfonate. Sulfonates also were obtained in similar reactions with 3-methylbutanesulfonyl chloride. Recently[7] the internal Friedel–Crafts reaction of ω-phenylalkanesulfonyl chlorides leading to cyclic sulfones was studied.

In view of the scarcity of information on the preparation of alkyl aryl sulfones by the Friedel–

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[1] An abstract of a thesis submitted by Calvin W. Vriesen to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1952.

[2] Purdue Research Foundation Fellow.

[3] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 673–675.

[4] R. Otto, *Ber.*, **13**, 1287 (1880).

[5] J. Böeseken and H. W. van Ockenburg, *Rec. trav. chim.*, **33**, 320 (1914).

[6] H. Burton and E. Hoggarth, *J. Chem. Soc.*, 14 (1945).

[7] W. E. Truce and J. P. Milionis, THIS JOURNAL, **74**, 974 (1952).

Crafts method, the behavior under various conditions of the simplest member of the series, methanesulfonyl chloride, was studied. Benzene was selected for this controlled study since it can give only one monosubstituted product and since with substituted benzenes, there could be the added complication of substituent groups migrating under the acidic conditions.

The relative efficacy of certain Friedel–Crafts catalysts is shown in Fig. 1. Aluminum chloride, antimony pentachloride and ferric chloride were selected since they have been shown to be the most efficient catalysts in the acetylation of toluene.[8] The comparison is based on the amount of methyl phenyl sulfone actually isolated. The reactions were conducted for the indicated times at reflux temperature; one equivalent of catalyst was employed and an excess of benzene was used as solvent. As is indicated by the graph, aluminum chloride was found to be the most active catalyst for the reaction. The fact that the conversion attains a constant value after a sufficient time interval indicates that methyl phenyl sulfone does not undergo further reaction under these conditions. Aluminum bromide was found to be too vigorous a catalyst. Boron trifluoride could not be dissolved in the reaction mixture in equivalent amounts and presumably did not form a complex with methanesulfonyl chloride; no sulfone was isolated in this experiment. Acetyl chloride similarly does not form a stable complex with boron trifluoride under similar conditions.[9]

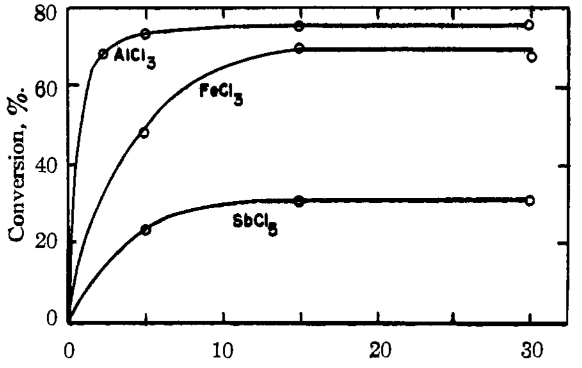


Fig. 1.—Conversion of CH_3SO_2Cl + C_6H_6 to $CH_3SO_2C_6H_5$ as a function of reflux time.

The results obtained by varying the amount of catalyst are shown in Fig. 2. The same reaction conditions were utilized as in the first study, but the time of reaction was held constant at fifteen hours. The graph shows that an excess of aluminum chloride results in a marked decrease in the conversion to methyl phenyl sulfone. Böeseken[5] used an excess of aluminum chloride, which affords an explanation for the fact that his conversion was "not large." Evolution of sulfur dioxide was noted when the reaction was carried out in the presence of two equivalents of aluminum chloride. It may be that the sulfonyl chloride–aluminum chloride complex reacts with additional aluminum chloride as

$$CH_3SO_2Cl\cdot AlCl_3 \xrightarrow{AlCl_3} CH_3Cl\cdot AlCl_3 + AlCl_3\cdot SO_2$$

An aluminum chloride–sulfur dioxide complex has been prepared.[10] Ferric chloride, a weaker acid, apparently does not bring about a similar decomposition.

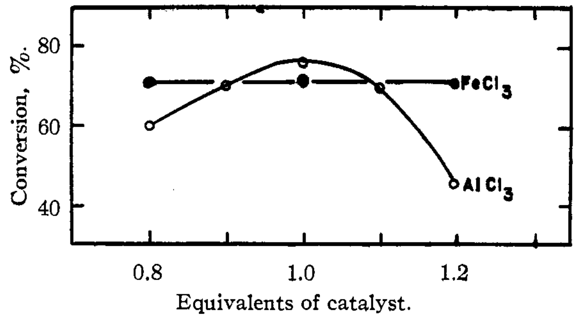
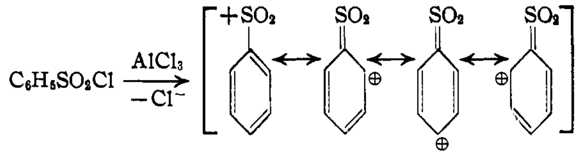


Fig. 2.—Conversion of CH_3SO_2Cl + C_6H_6 to $CH_3SO_2C_6H_5$ as a function of the amount of catalyst; reflux time 15 hr.

The ease with which various sulfonyl chlorides decompose in the presence of Friedel–Crafts type catalysts is probably a function of the stability of the sulfonyl ion on the one hand and the stability of the corresponding carbonium ion on the other. For example, considerable resonance stabilization of an aromatic sulfonyl ion would be expected, *e.g.*



This effect plus the inability of the resulting phenylcarbonium ion to stabilize itself by resonance hinders the occurrence of the dissociation

$$C_6H_5SO_2^+ \xrightarrow{AlCl_3} C_6H_5^+ + SO_2$$

An excess of aluminum chloride was used in most of the reactions that have been reported for aromatic sulfonyl chlorides,[8] and the excess catalyst appeared to have no deleterious effect.

On this basis, one would expect the ion, $CH_3SO_2^+$, to be less stable than the benzenesulfonyl ion. In fact the methanesulfonyl chloride–aluminum chloride complex decomposes to methyl chloride and sulfur dioxide when it is heated gently.[5] Other applications of this hypothesis can be cited. Phenylmethanesulfonyl chloride will decompose to benzyl chloride and sulfur dioxide when it is heated slightly over its melting point.[11] Here the sulfonyl ion is not appreciably stabilized by resonance, while the benzylcarbonium ion is stabilized by resonance. Another example is the instability of 1-phenyl-3-butanesulfonyl chloride,[12] which loses sulfur dioxide even at refrigerator temperature. The driving force for this decomposition is presumably the

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(8) O. C. Dermer, D. M. Wilson, F. M. Johnson and V. H. Dermer, THIS JOURNAL, **63**, 2881 (1941).

(9) H. C. Brown, H. I. Schlesinger and A. B. Burg, *ibid.*, **61**, 673 (1939).

(10) O. Ruff, *Ber.*, **35**, 4453 (1902).

(11) H. Limpricht, *Ber.*, **6**, 534 (1873).

(12) The preparation of this substance was carried out by B. K. Meyer of this Laboratory.

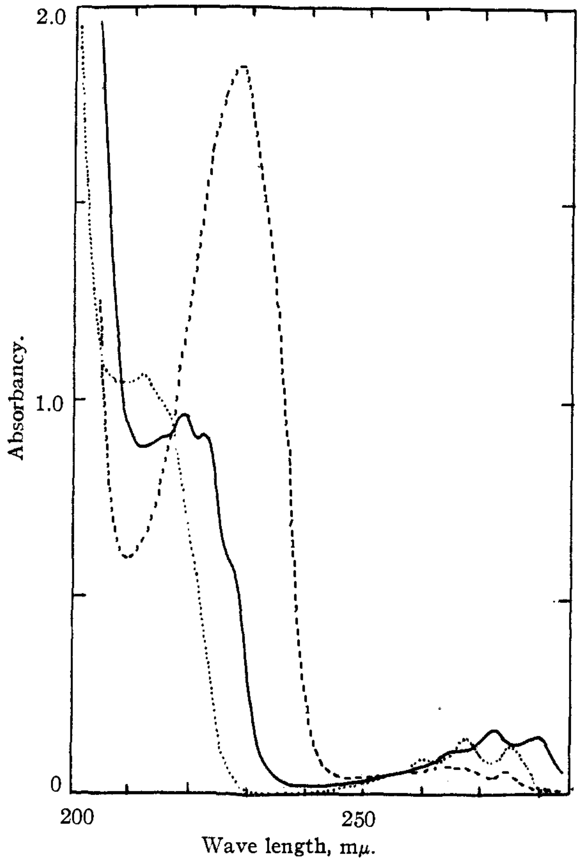

Fig. 3.—Ultraviolet spectra of chlorophenyl methyl sulfones; cell depth, 1 cm.; reference cell, 95% EtOH.

Legend	Chlorophenyl methyl sulfone	Concn., moles/l. × 10^4
———	Ortho	1.09
....	Meta	1.22
- - - -	Para	1.18

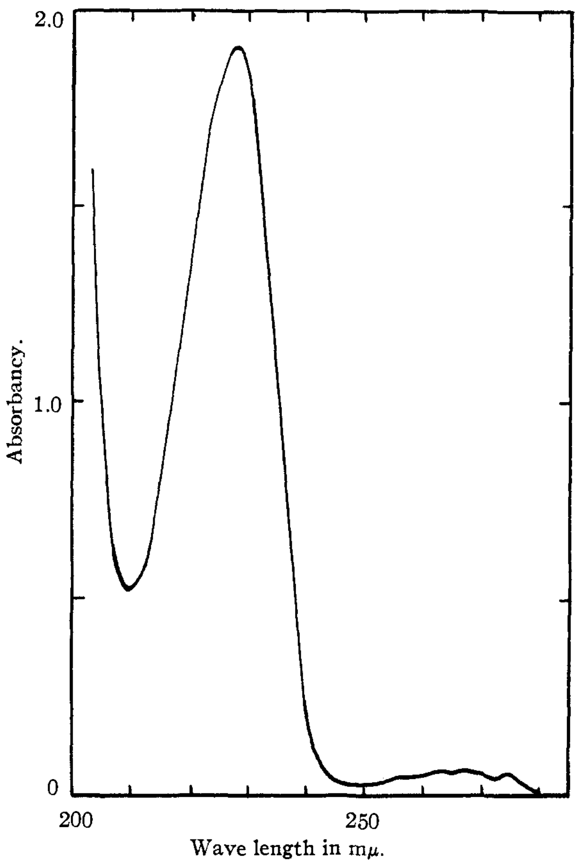

Fig. 4.—Ultraviolet spectrum of purified Friedel–Crafts product from chlorobenzene; cell depth, 1 cm.; reference cell, 95% EtOH; concn., 1.28 × 10^{-4} molar.

greater stability of a secondary carbonium ion over that of a primary carbonium ion.[13]

The result of a study of the effect of solvents indicates that a satisfactory solvent is an excess of the hydrocarbon being substituted. The methanesulfonyl chloride–aluminum chloride complex is insoluble in carbon disulfide and petroleum ether and consequently these solvents cannot be used to advantage. Also, the Perrier procedure[14] cannot be applied. Ethylene chloride and *sym*-tetrachloroethane are unsatisfactory since they must be handled at relatively low temperature in the presence of aluminum chloride. Nitrobenzene is somewhat unsatisfactory as a solvent because of the difficulty entailed in its removal from the reaction mixture. Steam distillation cannot be utilized because of the steam volatility of methyl phenyl sulfone. When 1-nitropropane was used as a solvent, decomposition occurred under the conditions of the reaction. When one equivalent of 1-nitropropane was added to the reaction conducted in excess benzene, conversions of the same order of magnitude were obtained as with excess benzene alone, but the time of reaction was increased. The maximum conversion, 76.8%, was obtained when excess benzene was used as the solvent, when the reaction mixture was heated for 15 hours at steam-bath temperature, and when one equivalent of aluminum chloride was used as the catalyst.

The reaction with toluene in the presence of aluminum chloride resulted in an oily mixture of isomers, which distilled at 133–141° (3 mm.) and whose composition was that of methyl tolyl sulfone. Examination of the boiling points of the individual isomers indicated that they could not be separated by distillation. Therefore, spectral analysis was employed to determine that approximately 15% and 36% of the product constituted the *m*-isomer and the *p*-isomer, respectively.

The reaction of methanesulfonyl chloride with chlorobenzene afforded the *p*-isomer in good yield. Ultraviolet spectra indicated for the crude product a purity of 88%, and 95% for the once-recrystallized product (Figs. 3 and 4). Furthermore, the Friedel–Crafts product and the independently prepared *p*-isomer melted at 96.5–98.0°, and considerable depression was noted when the pure *m*- and *o*-isomers were admixed. Bromobenzene and fluorobenzene likewise gave *p*-substituted phenyl methyl sulfones as the only isolated products.

The reaction of anisole in the presence of stannic chloride resulted in demethylation and the formation of phenyl methanesulfonate. A similar result was noted by Burton and Hoggarth[6] when they treated hydroquinone methyl ether with methane-

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[13] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 41.

[14] G. Perrier, *Bull. soc. chim.*, **31**, 859 (1904).

sulfonyl chloride in the presence of zinc chloride. However, with aromatic sulfonyl chlorides, the normal Friedel–Crafts reaction appears to occur rapidly enough to prevent demethylation and esterification. Presumably, with methanesulfonyl chloride, the rate of forming the attacking particle is exceeded by the rate of demethylation. The reaction with mesitylene in the presence of stannic chloride resulted in a small amount of product. The slow rate of formation of the attacking particle is apparently exceeded by the rate of decomposition and polymerization of mesitylene in the presence of Friedel–Crafts catalysts. On the other hand, satisfactory conversions are obtained with aromatic sulfonyl chlorides[15]; here the rate of formation of the attacking particle exceeds the rate of decomposition of mesitylene.

The para/meta ratio of 2.4 for the reaction of toluene indicates that the attacking particle, once formed, is a comparatively vigorous reagent of low selectivity.[16] The ratio of 3.7 for the rates of reaction of *p*-bromobenzenesulfonyl chloride with toluene and benzene[17] is additional evidence for the relatively high activity of "sulfonyl ions." That no isomerization to the *m*-isomer occurred during the reaction is evidenced by the fact that when methyl *p*-tolyl sulfone is treated with hydrogen chloride and aluminum chloride and heated on the steam-bath for 1.5 hours (the conditions employed in the Friedel–Crafts reaction) it is recovered unchanged.

The results with chlorobenzene indicate that the chloro substituent strongly orients the entering group, despite the low selectivity of the reagent. This is in accord with the reactions of *o*-chlorotoluene, where electrophilic substitutions predominantly occur para to the chloro group.[18] To determine whether any rearrangement occurred in this Friedel–Crafts reaction, *m*-chlorophenyl methyl sulfone was treated with hydrogen chloride and aluminum chloride for seven hours, but it was recovered unchanged.

Experimental

Friedel–Crafts Reaction of Methanesulfonyl Chloride with Benzene.—The conversions obtained in this study are shown in Fig. 1. Ten grams (0.0874 mole) of methanesulfonyl chloride, b.p. 46–48°, was added to 11.7 g. (0.0874 mole) of anhydrous aluminum chloride or 14.2 g. (0.0874 mole) of anhydrous ferric chloride in 25 ml. of dry benzene and the reaction mixtures were heated on the steam-bath for the times indicated in the graph. In the experiments with antimony pentachloride, 26.1 g. (0.0874 mole) of the catalyst was added to a solution of 10.0 g. of methanesulfonyl chloride in 25 ml. of benzene. In the experiments with aluminum chloride and ferric chloride, the reagents were mixed at room temperature since there was no vigorous initial reaction, but it was necessary to cool the reaction mixture with an ice-bath during the addition of antimony pentachloride. No stirring was necessary, since the complexes of methanesulfonyl chloride were soluble in the aromatic hydrocarbons. The reaction mixtures were decomposed by pouring into ice–hydrochloric acid mixtures. Excess benzene was removed by evaporation under an air stream and the methyl phenyl sulfone was treated with charcoal and recrystallized from water; m.p. 84–85°, lit. 88°.[5]

Decomposition occurred and no sulfone was isolated when 11.6 g. (0.044 mole) of aluminum bromide was added to 5.00 g. (0.044 mole) of methanesulfonyl chloride in 15 ml. of benzene and the reaction mixture was heated on the steam-bath for 2 hours.

Only about 0.5 equivalent (1.4 g.) of boron trifluoride would dissolve in a solution of 5.0 g. (0.044 mole) of methanesulfonyl chloride in 15 ml. of benzene at room temperature. No sulfone was isolated from the reaction mixture after it had been heated on the steam-bath for 28 hours.

The effects of varying the amounts of catalysts are shown in Fig. 2. The reaction mixtures were heated on the steam-bath for 15 hours. Isolation and purification was carried as above.

Various solvents were examined as is shown in Table I. The amount of methanesulfonyl chloride and aluminum chloride used was 0.0874 mole each.

TABLE I

THE EFFECT OF SOLVENT IN THE FRIEDEL–CRAFTS REACTION OF METHANESULFONYL CHLORIDE WITH BENZENE

Time at steam-bath temp., hr.	Solvent	Result
6	Carbon disulfide	2.8% conversion
14	1-Nitropropane	Decomposition
5	1-Nitropropane (0.0874 mole) + benzene (excess)	65% conversion
15		67% conversion
30		70% conversion

Friedel–Crafts Reaction of Methanesulfonyl Chloride with Toluene.—Methanesulfonyl chloride (80.2 g., 0.70 mole) was added to 93.3 g. (0.70 mole) of aluminum chloride suspended in 150 ml. of toluene and the reaction mixture was heated on the steam-bath for one hour. The reaction mixture was decomposed by pouring into ice-water and the layers were separated. Additional extraction of the water layer was carried out with benzene. The organic layer was washed with dilute sodium carbonate solution followed by water, and it was dried over calcium chloride. The excess toluene and benzene were removed and distillation of the residual oil at 133–141° (3 mm.) resulted in 62 g. (52%) of product.

A Perkin–Elmer double beam recording spectrophotometer (No. 21) with a sodium chloride prism was utilized to record the spectra of the three isomers in acetone solution. Initial calculations indicated the presence of 15% of the *m*-isomer (no peaks were available for the analysis of the *o*- and *p*-isomers in acetone, carbon tetrachloride or chloroform). The value for the *m*-isomer was verified by comparing the spectrum of a synthetic mixture of the isomers containing 15% of the *m*-isomer with the spectrum of the Friedel–Crafts product. The ultraviolet spectra (Fig. 5) of the three isomers in 95% ethanol were recorded on a Cary recording spectrophotometer (Model 10–11M). The amount of *p*-isomer present was calculated at 36 ± 3% by determinations made at 208, 225 and 270 mμ.

Authentic Samples of the Methyl Tolyl sulfones.—Following a general procedure,[19] 6.9 g. (0.30 mole) of sodium was dissolved in a mixture of 38 g. (0.30 mole) of *o*-thiocresol and 100 ml. of ethanol. Methyl iodide (50 g., 0.35 mole) was added gradually and the reaction mixture was refluxed for 30 minutes on the steam-bath and then left to stand overnight at room temperature. The reaction mixture was poured into 800 ml. of water and extracted with chloroform, and the chloroform was dried over calcium chloride. Distillation resulted in 26 g. (62%) of product boiling at 211.5–213.0° (743 mm.), n^{20}_{D} 1.5796.

Anal. Calcd. for $C_8H_{10}S$: C, 69.51; H, 7.29. Found: C, 69.65; H, 7.39.

Oxidation of *o*-tolyl methyl sulfide in glacial acetic acid with 30% hydrogen peroxide[20] gave a product with m.p. 55.0–57.4° after recrystallization from ethanol–water; lit.[21] oil, b.p. 133–134° (3 mm.).

Methyl iodide (36 g., 0.25 mole) was added gradually to 5.3 g. (0.23 mole) of sodium dissolved in 29 g. (0.23 mole) of

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(15) M. E. Maclean and R. Adams, THIS JOURNAL, **55**, 4683 (1933).

(16) H. C. Brown *et al.*, *Ind. Eng. Chem.*, **45**, 1462 (1953).

(17) S. C. J. Olivier, *Rec. trav. chim.*, **33**, 91 (1914).

(18) A. F. Hollemann, *Chem. Revs.*, **1**, 189 (1924).

(19) E. Bourgeois and A. Abraham, *Rec. trav. chim.*, **30**, 413 (1911).

(20) H. Gilman and H. S. Broadbent, THIS JOURNAL, **69**, 2053 (1947).

(21) J. Traeger and W. Voigtlaender-Tetzner, *J. prakt. Chem.*, **54**, 524 (1806).

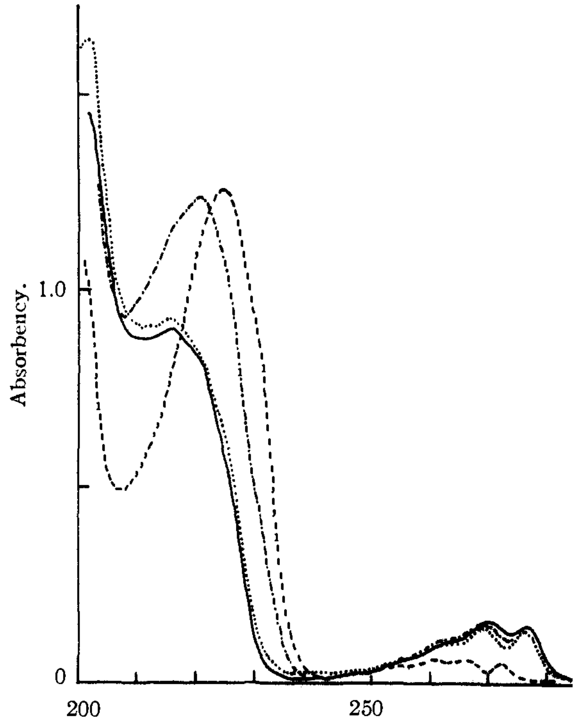

Fig. 5.—Ultraviolet spectra of methyl tolyl sulfones and of Friedel–Crafts product; cell depth, 1 cm.; reference cell, 95% EtOH.

Legend	Substance	Concn., moles/l. × 10⁴
———	Methyl *o*-tolyl sulfone	1.00
....	Methyl *m*-tolyl sulfone	1.13
----	Methyl *p*-tolyl sulfone	1.00
.-.-.-.	Friedel–Crafts product	1.46

m-thiocresol and 80 ml. of absolute ethanol; 19 g. (61%) of crude product was obtained. Oxidation of crude methyl *m*-tolyl sulfide in glacial acetic acid with 30% hydrogen peroxide gave an oil, after dilution of the reaction mixture with water. Distillation at 137–138° (3 mm.) gave a product with m.p. 34–35° after recrystallization from petroleum ether.

Anal. Calcd. for $C_8H_{10}O_2S$: C, 56.44; H, 5.92. Found: C, 56.31; H, 5.98.

Sodium *p*-toluenesulfinate (37 g., 0.20 mole) and 36 g. (0.25 mole) of methyl iodide in 100 ml. of ethanol were refluxed for 17 hours. The product, which was isolated after diluting the reaction mixture with water and distilling at 139–140° (3 mm.), weighed 17 g. (51%), m.p. 88°, lit. 86–87°.[22]

Friedel–Crafts Reaction of Methanesulfonyl Chloride with Halobenzenes.—Ten grams (0.0874 mole) of methanesulfonyl chloride was added to 11.7 g. (0.0874 mole) of aluminum chloride in 25 ml. of chlorobenzene and the reaction mixture was heated on the steam-bath for 6 hours. The reaction mixture was decomposed by pouring into ice-water. Separation of the aqueous layer and evaporation of the excess chlorobenzene under an air stream followed by recrystallization from aqueous ethanol resulted in 12 g. (72%) of a crude product with m.p. 75–84°. Treatment with charcoal and another recrystallization from aqueous ethanol resulted in 10 g. (60%) of product with m.p. 96.5–98°, lit.[23] 96°, no depression in m.p. on admixture with authentic sample[23] of methyl *p*-chlorophenyl sulfone. Authentic samples[23] of the meta (m.p. 105–106°) and the ortho (m.p. 89–90°) isomers were also prepared.

Ten grams (0.0874 mole) of methanesulfonyl chloride was added to 11.7 g. (0.0874 mole) of aluminum chloride in 25 ml. of bromobenzene and the mixture was heated on the steam-bath for 7 hours. Isolation and purification as with chlorobenzene resulted in 11.5 g. (56%) of product, m.p. 101.5–103.0°, no depression on admixture with an authentic sample[24] of methyl *p*-bromophenyl sulfone.

Five grams (0.044 mole) of methanesulfonyl chloride was added to 5.83 g. (0.04 mole) of aluminum chloride in 15 ml. of fluorobenzene and the reaction mixture was heated on the steam-bath for 7 hours. The reaction mixture was decomposed by pouring into ice-water. Removal of the excess fluorobenzene left 5.5 g. (73%) of product, m.p. 78–80° after recrystallization from water.

Following the procedure of Hann,[25] a mixture of 15 g. (0.16 mole) of fluorobenzene and 22.5 g. (0.17 mole) of aluminum chloride in 60 ml. of carbon disulfide was treated in turn with hydrogen chloride and sulfur dioxide. The salt obtained was refluxed for 16 hours with 22.5 g. (0.16 mole) of methyl iodide in 85 ml. of ethanol and 9.6 g. (36%) of product was obtained, m.p. 78–79°, mixed m.p. with Friedel–Crafts product 77–80°.

Anal. Calcd. for $C_7H_7O_2FS$: C, 48.26; H, 4.05. Found: C, 48.36; H, 4.09.

Friedel–Crafts Reaction of Methanesulfonyl Chloride with Anisole.—Ten grams (0.0874 mole) of methanesulfonyl chloride was added to 22.8 g. (0.0874 mole) of stannic chloride in 30 ml. of anisole and the reaction mixture was allowed to stand at room temperature for 3.5 days. It was then heated on the steam-bath for 52 hours. Removal of the solvent and recrystallization from ethanol–water resulted in 12.4 g. (76%) of product with m.p. 58–60°; mixed m.p. with authentic sample[26] of phenyl methanesulfonate (m.p. 59–61°) was 59–61°.

Friedel–Crafts Reaction with Mesitylene.—Five grams (0.043 mole) of methanesulfonyl chloride was added to 11.4 g. (0.043 mole) of stannic chloride in 15 ml. of mesitylene and the reaction mixture was allowed to stand at room temperature for 3.5 days and was then heated on the steam-bath for 26 hours. Removal of excess mesitylene by steam distillation resulted in 0.44 g. (5%) of product. Decolorization with charcoal and recrystallization from methanol gave a product melting at 128.5–130.0°, lit. 131–132°.[27] A mixed m.p. with an authentic sample of mesityl methyl sulfone (127.5–129°) was 127.5–130°.

Attempted Rearrangement of Methyl *p*-Tolyl Sulfone and *m*-Chlorophenyl Methyl Sulfone.—Seven grams (0.041 mole) of methyl *p*-tolyl sulfone was dissolved in 30 ml. of toluene, and 5.5 g. (0.041 mole) of aluminum chloride was added. Dry hydrogen chloride was passed into the reaction mixture while it was heated on the steam-bath for 1.5 hours. This was followed by isolation of 6.8 g. (97%) of sulfone, m.p. 87°.

m-Chlorophenyl methyl sulfone (4.08 g., 0.022 mole) was dissolved in 18 ml. of chlorobenzene and 2.88 g. (0.022 mole) of aluminum chloride was added. Dry hydrogen chloride was passed into the reaction mixture while it was heated on the steam-bath for 7 hours. The product isolated melted sharply at 106°.

LAFAYETTE, INDIANA

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[22] R. Otto, *Ber.*, **18**, 161 (1885).

[23] H. R. Todd and R. L. Shriner, THIS JOURNAL, **56**, 1382 (1934).

[24] R. F. Twist and S. Smiles, *J. Chem. Soc.*, **127**, 1252 (1925).

[25] R. M. Hann, THIS JOURNAL, **57**, 2167 (1935).

[26] F. Reverdin and P. Crepieux, *Ber.*, **35**, 1439 (1902); C. Schall, *J. prakt. Chem.*, **48**, 244 (1893).

[27] E. A. Fehnel and M. Carmack, THIS JOURNAL, **72**, 1292 (1950).