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Chlorinations with Sulfuryl Chloride. III. (a) The Peroxide-Catalyzed Chlorination of Aliphatic Acids and Acid Chlorides. (b) The Photochemical Sulfonation of Aliphatic Acids

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In an earlier paper[2] it was shown that various types of hydrocarbons can be chlorinated rapidly and conveniently by sulfuryl chloride in the presence of a small quantity of an organic peroxide. It was suggested that the reaction depends upon the initiation by the peroxide of a chain reaction involving chlorine atoms.

We have extended the study of the action of sulfuryl chloride to other types of organic compounds. The present paper is devoted to the chlorination of aliphatic acids and acid chlorides and to a preliminary report of the photochemical sulfonation of aliphatic acids.

Chlorination of Acids and Acid Chlorides

In the dark and in the absence of catalysts sulfuryl chloride does not react with aliphatic acids or acid chlorides to any appreciable extent at temperatures as high as the boiling point of the reaction mixtures (70–90°). In the presence of a small quantity of peroxide, however, chlorination of acids and acid chlorides takes place readily. Acetic acid and acetyl chloride, however, are exceptions to this generalization.

The chlorination of acids and acid chlorides by this method has been carried out, for the most part, in accordance with the general procedure described in the first paper of this series.[2] A slight modification of this procedure, however, was found to be advisable. Except in the case of acetic acid, the chlorination of the carboxylic acids is a vigorous reaction, and it was found desirable to add a small quantity of a diluent. The acid chlorides react much less violently, and the addition of a diluent is unnecessary.

In the absence of added peroxides, acetic acid is not chlorinated to any extent by sulfuryl chloride. Upon heating of a mixture of the two compounds in the dark, the sulfuryl chloride under the catalytic influence of the acid is slowly dissociated into sulfur dioxide and chlorine, and the acetic acid can be recovered unchanged. In the presence of an added peroxide, chlorination occurs. The yield of chloroacetic acid, however, is poor compared to the almost quantitative yields which can be obtained in the chlorination of the higher homologs of acetic acid. Even under optimum conditions, the yield of chloroacetic acid is not greater than 50%[3] because of loss of sulfuryl chloride by dissociation.

Acetyl chloride differs even more from its higher homologs than does acetic acid: the compound cannot be chlorinated to any appreciable extent by the use of sulfuryl chloride and either lauroyl or benzoyl peroxide. This inactivity cannot be due to the low boiling point of acetyl chloride since addition of chlorobenzene to the reaction mixture (to raise the boiling point) has no effect, while addition of cyclohexane or toluene leads immediately to a vigorous reaction in which chlorination of the hydrocarbon occurs.

In marked contrast to the inactivity of acetic acid and acetyl chloride to the reagent, is the action of trimethylacetic acid and its acid chloride. These compounds, which are usually considered to be very unreactive toward substituting reagents, are chlorinated with remarkable ease by sulfuryl chloride in the presence of benzoyl peroxide. The beta chloro derivatives are formed.

Propionic acid and propionyl chloride are chlorinated readily by the reagent to yield both the alpha and the beta chloro isomers with the beta in excess.

The preferential chlorination of an aliphatic acid or acid chloride in the beta position is rather unusual in view of the emphasis usually placed upon the activity of the alpha position in these compounds. However, the study of the chlorination of *n*-butyric acid and isobutyric acid and the corresponding acid chlorides has established the fact that the above instance is no exception. In all the cases that we have investigated, *substitution takes place preferentially on a carbon atom which is some distance removed from the carboxyl group, with the result that the yields of beta or beta and gamma chlorinated derivatives which are obtained far exceed the amount of the alpha isomer.*

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[1] Eli Lilly Fellow, 1938–1939.

[2] Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

[3] The yields are based on the sulfuryl chloride.

The relative yields of isomers obtained in these reactions are listed in Table I.

TABLE I

PRODUCTS OF THE CHLORINATION OF ALIPHATIC ACIDS AND ACID CHLORIDES BY SULFURYL CHLORIDE AND PEROXIDES

Compound chlorinated	Products
Propionic acid	45% α-chloropropionic acid
	55% β-chloropropionic acid
Propionyl chloride	40% α-chloropropionyl chloride
	60% β-chloropropionyl chloride
Isobutyric acid	15% α-chloroisobutyric acid
	85% β-chloroisobutyric acid
Isobutyryl chloride	20% α-chloroisobutyryl chloride
	80% β-chloroisobutyryl chloride
n-Butyric acid	10% α-chloro-*n*-butyric acid
	45% β-chloro-*n*-butyric acid
	45% γ-chloro-*n*-butyric acid
n-Butyryl chloride	15% α-chloro-*n*-butyryl chloride
	55% β-chloro-*n*-butyryl chloride
	30% γ-chloro-*n*-butyryl chloride

An examination of the effect of the ordinary chlorination catalysts upon mixtures of sulfuryl chloride and organic acids or acid chlorides yielded more conventional results. For example, the addition of iodine to a reaction mixture of propionyl chloride and sulfuryl chloride kept at 70° initiates a slow reaction. The alpha chloro derivative was the only product which was isolated.

Results similar to those obtained in the peroxide-catalyzed reaction have been reported in the *photochemical* chlorination of carefully purified acids and acid chlorides in the absence of halogen carriers.[4] On the other hand, the chlorination of aliphatic acids and acid chlorides with the aid of halogen carriers as catalysts yields only the alpha-substituted derivatives.[5]

Obviously different mechanisms must operate in reactions giving such divergent products. Our entire experience suggests that both the photochemical chlorination and the peroxide-catalyzed reaction with sulfuryl chloride (which, alike, favor substitution in positions of the carbon chain other than the alpha) proceed through chain mechanisms involving chlorine atoms; on the other hand, chlorination of acids and acid chlorides with the aid of halogen carriers (in which substitution takes place only in the alpha position) must involve the action of some other form of active chlorine[6] upon the organic compound.

If, as seems probable, the active agent in the peroxide-catalyzed reactions of sulfuryl chloride is the chlorine atom, the explanation for the fact that the alpha position is not substituted to a degree commensurate with that calculated on a statistical basis is to be sought in the deactivating effect of the carboxyl and the acid chloride groups on the carbon–hydrogen bonds at the alpha position.

This is substantiated by the facts that neither the carboxyl nor the acid chloride groups can inhibit the peroxide-catalyzed reaction of sulfuryl chloride with other substances,[7] and observations that the sensitivity of the carbon–hydrogen bond to attack by chlorine atoms can be markedly decreased by substituents on an adjacent carbon atom. Thus, (1) secondary hydrogen atoms are substituted more readily than primary, (2) substitution of a second chlorine atom upon a carbon atom already holding a halogen substituent is difficult, and (3) a second chlorine atom tends to substitute a point on the carbon chain as far removed from the first chlorine substituent as possible.

The inertness of acetyl chloride toward chlorine atoms (produced from sulfuryl chloride and a peroxide) is therefore interpreted on the basis of a combined effect of the relatively high energy of activation and dissociation of primary hydrogen–carbon bonds and the further deactivation of these bonds induced by the acid chloride group. This suggestion is further supported by the fact that methyl chloroform also does not undergo the peroxide-catalyzed reaction with sulfuryl chloride.

Sulfonation of Aliphatic Acids

As has been mentioned, aliphatic acids do not react with sulfuryl chloride in the absence of catalysts and light. If light is not excluded, however, reaction occurs, leading not to chlorination but to sulfonation of the acid. In this way we have been able to prepare β-sulfopropionic acid and a sulfobutyric acid from the action of sulfuryl chloride on the corresponding acids.

The direct sulfonation of aliphatic acids and acid chlorides in the past has been accomplished by the action of sulfur trioxide or chlorosulfonic

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(4) Michael and Garner, *Ber.*, **34**, 4046 (1901).

(5) Markownikow, *Ann.*, **153**, 241–242 (1870); Wolffenstein and Rolle, *Ber.*, **41**, 735–736 (1908); Bass, U. S. Patent 2,010,685. In the case of the aliphatic acids of high molecular weight, such as stearic acid, it is reported that treatment with chlorine yields a mixed product; the rule that substitution takes place predominantly in the alpha position no longer holds.

(6) This problem will be taken up in detail in a forthcoming publication.

(7) Kharasch and Brown, THIS JOURNAL, **61**, 2148 (1939). Furthermore, the presence of an equimolar portion of acetyl chloride does not prevent the chlorination of either cyclohexane or toluene; the acetyl chloride acts only as an inert diluent.

acid upon the organic compound. In all cases, the product formed is reported to be the alpha sulfo derivative.

On the other hand, the photochemical sulfonation of aliphatic acids mentioned above does not lead to the alpha sulfo derivative. Indeed, a careful study of the product obtained from the action of sulfuryl chloride on propionic acid[8] indicates that the only sulfopropionic acid formed is the beta derivative. Thus, here again is an example of different mechanisms favoring different positions for substitution: attack of acids by reagents through what appears to be an ionic mechanism leads predominantly to alpha substitution, while attack through an atomic or free-radical mechanism favors beta substitution.

The generality of this sulfonation reaction of aliphatic acids was investigated, and it was found that while acetic acid does not react, *n*-butyric and isovaleric acids can be sulfonated by this means. The yields are somewhat poorer than that obtained with propionic acid. The position of the sulfonic acid group in these products was not established.

This reaction, photochemical sulfonation with sulfuryl chloride, appears to be catalyzed by the carboxyl group. This view is based upon the observation that aliphatic hydrocarbons can be sulfonated by sulfuryl chloride in the presence of acetic acid. The yields, however, are poor, indicating that the carboxylic acids are comparatively inefficient catalysts for this reaction. Since more efficient catalysts are now available,[9] the study of this catalytic activity of organic acids was not extended.

Experimental Part

Apparatus and Materials.—The types of reaction vessels and fractionating columns which were used in this work are described in an earlier article.[2] The acids used were either Eastman Kodak Co. or commercial chemicals with one exception, trimethylacetic acid.[10] The acid chlorides available commercially were not used: impurities present in these substances (volatile sulfur and phosphorus compounds) could be removed only with difficulty. Pure acid chlorides were prepared more conveniently by the action of benzoyl chloride upon the corresponding acids.[11]

Chlorination of Acetic Acid.—The following experiments are typical of the attempts made to chlorinate acetic acid with sulfuryl chloride.

The reaction mixture, consisting of 36.0 g. of anhydrous acetic acid[12] (0.6 mole) and 40.5 g. of sulfuryl chloride (0.3 mole), was refluxed in the dark for two hours, until evolution of gas ceased. Fractionation of the reaction mixture yielded better than 90% recovery of acetic acid (b. p. 117–119°). The formation of chloroacetic acid could not be demonstrated.

A similar reaction mixture of acetic acid and sulfuryl chloride was made up, and benzoyl peroxide (0.75 g., 0.003 mole) was added. Upon heating of this mixture a vigorous reaction occurred and was complete in fifty minutes. Fractionation of the product indicated a 30% yield of chloroacetic acid (b. p. 106–109° at 40 mm.).

An attempt was made to improve the yield by adding a diluent. The reaction mixture consisted of 36.0 g. of acetic acid, 40.5 g. of sulfuryl chloride, 0.75 g. of benzoyl peroxide, and 92.4 g. of carbon tetrachloride (0.6 mole). Refluxing of the reaction mixture initiated a slow reaction. At the end of three hours, and again at the end of six hours, 0.75-g. portions of benzoyl peroxide were added. At the end of nine hours, the reaction was but 70% complete (on basis of loss of weight). The chloroacetic acid isolated amounted to 50% of the calculated yield.

Acetyl Chloride.—Acetyl chloride could not be induced to undergo the peroxide-catalyzed reaction. Since the results are negative, the experiments need not be described in any detail. One reaction mixture, consisting of equimolar parts of sulfuryl chloride and acetyl chloride, was heated for twenty-four hours in the presence of 2 mole per cent. of benzoyl peroxide without effect. Addition of solvents (carbon tetrachloride, chlorobenzene) was unavailing. The inactivity cannot be due to any inhibiting properties of the molecule since acetyl chloride can be used as an inert solvent in the chlorination of toluene or cyclohexane.

Propionic Acid and Propionyl Chloride.—Propionic acid and propionyl chloride are chlorinated readily by the reagent. The isomeric chloropropionyl chlorides can be separated easily by fractionation. Since this method of analysis cannot be utilized for the separation of the isomeric chloropropionic acids without considerable difficulty, these isomers were separated by fractionation only after they had been transformed into the corresponding acid chlorides.

The reaction mixture consisted of 59.2 g. of propionic acid (0.8 mole), 54.0 g. of sulfuryl chloride (0.4 mole), and 61.6 g. of carbon tetrachloride (0.4 mole). Benzoyl peroxide (0.5 g., 0.002 mole) was added, and the mixture was heated gently under reflux in the dark. After one and one-half hours, no more gas was evolved, and the reaction was considered complete. An excess of thionyl chloride was added (190.4 g., 1.6 moles) and the heating continued for four hours more. The carbon tetrachloride, excess thionyl chloride and propionyl chloride were distilled at atmospheric pressure; the remainder was fractionated at 100 mm. The relative yields[13] of α-chloro-

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[8] The sulfonation of this acid was studied most thoroughly because of the relatively high yields which can be obtained, and the ease of separation and identification of the two possible isomers.

[9] Kharasch and Read, THIS JOURNAL, **61**, 3089 (1939).

[10] "Organic Syntheses," Coll. Vol. I, 1932, p. 510.

[11] Brown, THIS JOURNAL, **60**, 1325 (1938).

[12] The acetic acid was heated under reflux with 10% of its weight of acetic anhydride for twenty-four hours, and then carefully distilled through an efficient fractionating column.

[13] The total yield of monochloropropionyl chlorides before separation was 75%. In the preparations reported in this paper (with the exception of acetic acid) the yields of monochlorinated derivatives which were obtained varied between 70 and 90% of the calculated (based on chlorine). Losses were chiefly due to the formation of higher chlorinated compounds and loss of sulfuryl chloride through the condenser.

propionyl chloride (b. p. 51–54° at 100 mm., $n^{20}D$ 1.440) and β-chloropropionyl chloride (b. p. 81–84° at 100 mm., $n^{20}D$ 1.454) were as 45 to 55.

The identities of the products were confirmed by the preparation of the anilides: α-chloropropionanilide, m. p. 91–92°, and β-chloropropionanilide, m. p. 119–120°.

The chlorination of propionyl chloride is a much slower reaction which requires four to six hours for completion.

Isobutyric Acid and Isobutyryl Chloride.—The chlorinations of isobutyric acid and isobutyryl chloride were carried out in a manner similar to those already described. The product first was fractionated under reduced pressure and then refractionated at atmospheric pressure. The analysis and identification of the products was complicated by the fact that the values of the boiling points of the two isomeric chloroisobutyryl chlorides reported in the literature are in error. Michael and Garner[14] report the boiling points of α- and β-chloroisobutyryl chlorides to be 126–127° and 171–172°, respectively. The distillation of the reaction products from our preparations yielded two fractions, b. p. 117–118° ($n^{20}D$ 1.4369) and 151–152° ($n^{20}D$ 1.4542). The lower-boiling of these products was identified as α-chloroisobutyryl chloride by transformation into the acid, m. p. 28–30°, and the preparation of the anilide, m. p. 71–71.5°. The anilide of the higher-boiling fraction, which must be the β-chloro derivative, was prepared; the derivative crystallized from alcohol and water in long prismatic needles, m. p. 109.0–109.5°.

Anal. Calcd. for $C_{10}H_{12}ONCl$: N, 7.1; Cl, 17.98. Found: N, 7.2; Cl, 18.01.

***n*-Butyric Acid and *n*-Butyryl Chloride.**—Both *n*-butyric acid and *n*-butyryl chloride reacted with great ease. The chlorination of 150–200 g. of these compounds was complete in less than one hour. The isomeric chlorinated acids were isolated as the acid chlorides (after treatment with thionyl chloride) by fractionation under reduced pressure. At a pressure of 40 mm., the alpha derivative was collected at 45–50°, the beta ($n^{20}D$ 1.4525) at 65–67°, and the gamma ($n^{20}D$ 1.4631) at 83–85°. The identities of the isomers were confirmed by the preparation of the *p*-toluides.[15]

Trimethylacetic Acid and Chloride.—The β-chlorotrimethylacetic acid was separated from the reaction mixture by fractionation under reduced pressure; the acid was collected at 126–129° at 30 mm. It crystallized from low-boiling ligroin in the form of plates melting at 40–42°. The identity of the product was established by a chlorine determination and the neutralization equivalent.

Anal. Calcd. for $C_5H_9O_2Cl$: Cl, 26.07; neut. equiv., 136.5. Found: Cl, 25.88; neut. equiv., 136.

The amide crystallized from water in the form of plates, m. p. 108–109°.

Anal. Calcd. for $C_5H_{10}ONCl$: N, 10.34. Found: N, 10.42.

The β-chlorotrimethylacetyl chloride, formed by the chlorination of trimethylacetyl chloride, was also isolated from the reaction mixture by fractionation (b. p. 85–86° at 60 mm., $n^{20}D$ 1.4539). The amide was prepared and found to be identical with that obtained from the chlorinated acid.

Chlorination of Propionyl Chloride (Effect of Halogen Carriers).—The reaction mixture was made up of 46.3 g. of propionyl chloride (0.5 mole) and 40.5 g. of sulfuryl chloride (0.3 mole). Iodine (0.5 g.) was added, and the mixture heated under reflux for twelve hours. The loss in weight of the reaction mixture was 80% of the calculated amount. Fractionation of the reaction mixture yielded 24.3 g. of material distilling in the range 103–110°. This material was treated with mercury to remove free iodine, and redistilled. The final yield was 22.0 g. of an acid chloride (b. p. 108–109°) which was identified as α-chloropropionyl chloride. The formation of the beta isomer could not be demonstrated.

Catalysts other than iodine were tested. Granulated animal charcoal causes complete dissociation of the sulfuryl chloride in five hours; however, less than 20% of chlorinated acid chloride was formed. Aluminum chloride, which is a very vigorous catalyst for the chlorination of aromatic nuclei with sulfuryl chloride, was unsatisfactory for this reaction. A mixture of iodine and carbon reduces the time required for the reaction to six hours and may therefore have some advantage over the use of iodine alone. In all cases the alpha isomer was the only chlorinated acid chloride which could be isolated.

Sulfonation of Propionic Acid.[16]—A mixture of 78.0 g. of propionic acid (1.0 mole) and 67.5 g. of sulfuryl chloride (0.5 mole) was heated gently under reflux for two hours. During the course of the reaction the flask was illuminated by a 300-watt lamp situated about 5 cm. from the reaction flask. After the reaction was complete, a mixture of ligroin (60–70°) and benzene was added, precipitating a white solid. The mixture was permitted to stand for twenty-four hours at room temperature to ensure complete precipitation. The supernatant liquid was then decanted, and the solid was washed several times with dry ligroin. Finally, the mixture was filtered on a Büchner funnel and the solid quickly transferred to a desiccator containing paraffin and phosphorus pentoxide. The weight of the dry crude product (m. p. 100–102°) was 28.3 g., a yield of 37%.

Its properties and reactions indicate that this substance must be β-sulfopropionic acid. The analysis and identification were rendered difficult by our inability to purify the product by recrystallization: the crude material was insoluble in ligroin, benzene and chloroform, and extremely soluble in water and alcohol to yield strongly acid solutions. The extreme hygroscopic nature of the substance added to the difficulties of analysis. A qualitative analysis showed the presence of sulfur and the absence of halogen.

Anal. Calcd. for $C_3H_6O_5S + {}^1/_2H_2O$ ($HO_3SC_2H_4COOH + {}^1/_2H_2O$): C, 22.09; S, 19.63; H, 4.3; neut. equiv., 81.5. Found: C, 22.11; S, 19.62; H, 4.7; neut. equiv., 80.6.

The water indicated in this analysis is probably not a definite quantity. It was noted that even very short exposures to the atmosphere rapidly increased the water content of the material.

The position of the sulfonic acid group was definitely established by a study of the solubility and composition of the barium salt. The barium salt of α-sulfopropionic

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(14) Michael and Garner, *Ber.*, **34**, 4054–4055 (1901).

(15) Wolffenstein and Rolle, *ibid.*, **41**, 736–737 (1908).

(16) These results are to be considered as a preliminary report; we are continuing the study of this reaction.

acid crystallizes from water with 1.5 moles of water and is soluble to the extent of 7 parts of salt per 100 parts of water. On the other hand, the barium salt of the β-isomer crystallizes with 5.0 moles of water and is less than one-tenth as soluble.

Ten grams of the dried sulfopropionic acid was dissolved in 300 cc. of hot water, and the solution was neutralized with crystalline barium hydroxide. The hot solution was filtered and permitted to cool to room temperature. The crystals which separated (prismatic plates) were collected on a filter and air dried. The filtrate was then concentrated to 100 cc. and the process was repeated. A total yield of 22.1 g. of the air-dried salt was obtained (first crop, 15.8 g.; second crop, 6.3 g.), representing slightly more than 90% of the yield theoretically possible.

Anal. Calcd. for $Ba(C_3H_4O_5S)\cdot 5H_2O$: H_2O, 23.73; Ba, 36.21. Found: H_2O, 23.57; Ba, 36.33.

In the course of the attempts to recrystallize the original product, it was found that treatment with thionyl chloride yielded a crystalline substance which has been tentatively identified as an anhydride of β-sulfopropionic acid.

Three grams of the crude sulfopropionic acid was heated under reflux for three hours with 20 g. of thionyl chloride. Ligroin was added, and the mixture was heated until the solid which at first had precipitated, redissolved. Upon cooling, a solid separated in the form of thin plates. This material was recrystallized from thionyl chloride and ligroin, and placed in a vacuum desiccator over paraffin and freshly fused potassium hydroxide. The substance melted sharply at 76–77°. It contained sulfur, but no chlorine. The neutralization equivalent was found to be 67.4, 68.3; the calculated value for the anhydride is 68.0.

Acids as Catalysts for Sulfonation of Hydrocarbons.[9]—Since the carboxyl group appears to be the active catalyst in this reaction, we studied the photochemical sulfonation of hydrocarbons in the presence of a carboxylic acid. Sulfonation occurs, but the yields are low. The following experiment is typical of the results obtained.

In a flask were placed 42.0 g. of cyclohexane (0.5 mole), 33.8 g. of sulfuryl chloride (0.25 mole) and 1.0 g. of acetic acid. The mixture was heated gently and illuminated for four hours. Upon fractionation, there was obtained 20 g. of cyclohexyl chloride (b. p. 65–70° at 60 mm.) and 2.2 g. of cyclohexane sulfonyl chloride (b. p. 125–135° at 12 mm.). The yield of sulfonyl chloride is but 5% of the calculated.

Summary

1. The action of sulfuryl chloride on acetic, propionic, *n*-butyric, isobutyric, and trimethylacetic acids and the corresponding acid chlorides under various conditions, has been investigated.

2. In the absence of catalysts and light sulfuryl chloride does not react with organic acids and acid chlorides.

3. In the presence of a small quantity of added peroxide, the higher aliphatic acids and acid chlorides react vigorously to form 70 to 90% yields of chlorinated derivatives. On the other hand, acetic acid reacts with difficulty, and acetyl chloride cannot be chlorinated in this way.

4. The yields of the various isomeric chloro derivatives indicate that the alpha position in the carbon chain is substituted with greater difficulty than the beta and gamma positions. That is, *the product consists chiefly of beta or beta and gamma chloro acids* (*or the corresponding acid chlorides*). For example, the chlorination of *n*-butyryl chloride yields 15% α-, 55% β-, and 30% γ-chlorobutyryl chloride.

5. If halogen carriers, such as iodine, instead of peroxides are used to catalyze the reaction of sulfuryl chloride with acid chlorides, substitution takes place only at the alpha position. The mechanisms involved in the two reactions must be of two different types; it appears that the peroxide-catalyzed reaction is a chain reaction involving chlorine atoms, while the iodine-catalyzed chlorination is due to another form of active chlorine.

6. Sulfuryl chloride also undergoes a photochemically catalyzed reaction with the higher aliphatic acids to yield sulfonated acids. In this way, a 37% yield of β-sulfopropionic acid readily can be isolated. *n*-Butyric and isovaleric acids also have been sulfonated. Acetic acid does not react.

7. Acetic acid catalyzes the photochemical sulfonation of hydrocarbons with sulfuryl chloride. The yield is small.

8. In the course of this investigation, the following compounds have been prepared and characterized: β-chlorotrimethylacetic acid and the corresponding acid chloride and amide, and the anhydride of β-sulfopropionic acid.

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