Sulfuryl chloride is a versatile reagent with great potentialities in organic syntheses. Under appropriate conditions it may be used for the chlorination and sulfonation of both aliphatic and aromatic derivatives. It may also be applied as an acylating and condensing agent. The simplicity of these reactions, their ease of control, and their high yields promise to make the reagent particularly useful in many applications which require simple and unspecialized equipment.

Sulfuryl Chloride

in

Organic Chemistry

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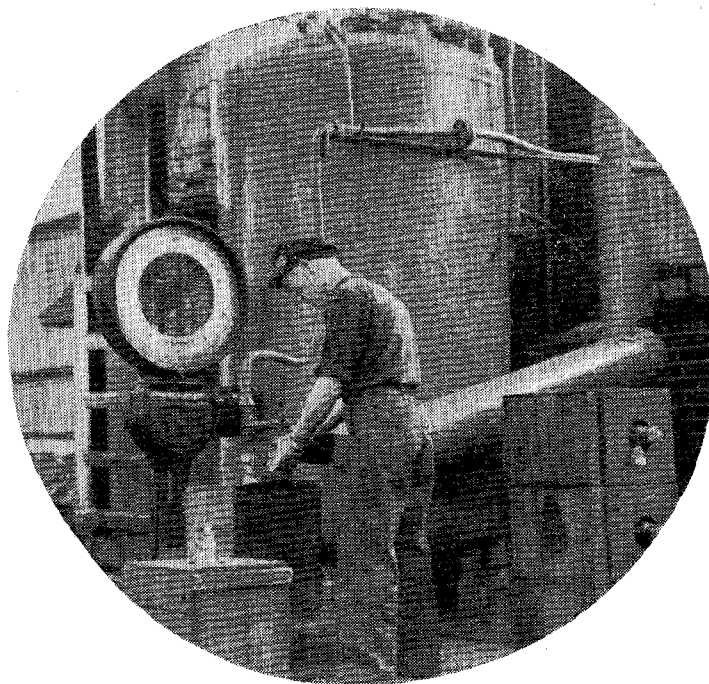
Filling Carboys from the Sulfuryl Chloride Stabilizer (Hooker Electrochemical Company)

THE use of sulfuryl chloride as a chlorinating agent for aromatic compounds dates back to the early days of organic chemistry. In 1866 the observation was made that phenol is easily chlorinated by sulfuryl chloride at room temperature and that benzene may be similarly chlorinated at somewhat higher temperatures. It was subsequently discovered that by suitable adaptation of the experimental conditions sulfuryl chloride could also be used as a sulfonating agent for aromatic compounds. Means have recently been found for extending these reactions to the aliphatic hydrocarbons and their derivatives. The potentialities of this versatile reagent are not limited to its use as a chlorinating and sulfonating agent. The acylation of alcohols and amines, the conversion of carboxylic acid salts to acid chlorides and anhydrides, and the facilitation of various condensation reactions are among the better known applications of sulfuryl chloride.

The ease with which these reactions may be controlled and directed is noteworthy. For example, in a mixture of an aromatic and a paraffinic or a cycloparaffinic hydrocarbon such as benzene and cyclohexane, it is possible either to chlorinate selectively or to sulfonate selectively one or the other hydrocarbon merely by changing the experimental conditions. Of particular interest at this time is the relative simplicity of the equipment needed. Some representative reactions of sulfuryl chloride are presented here to indicate its potentialities in organic chemistry; no exhaustive review is attempted.

CHLORINATION OF AROMATIC NUCLEI

Although sulfuryl chloride readily chlorinates the more reactive benzenoid derivatives, of which the phenols and amines are typical, it reacts with benzenoid hydrocarbons in the absence of catalysts only under rather vigorous treatment. Thus, to chlori-

nate benzene, Dubois heated the hydrocarbon with sulfuryl chloride in sealed tubes at 150° C. (*23*) and Töhl and Eberhard used a temperature of 160–170° (*70*).

In the course of a comprehensive investigation of the effect of various catalysts on the reaction between sulfuryl chloride and benzene, Silberrad found that substances commonly classed as halogen carriers (sulfur, iodine) bring about the chlorination of the benzene ring at lower temperatures (*65*). A mixture of sulfur monochloride and aluminum chloride is a particularly effective catalytic agent. A chlorinating reagent composed of 1% of this catalyst dissolved in sulfuryl chloride chlorinates benzene rapidly and smoothly in the cold (*66*). With this reagent stepwise polychlorination of benzene through the hexachloro derivative takes place under comparatively mild conditions.

Silberrad also reported that toluene may be similarly chlorinated in stages (*67*), and that unlike other powerful chlorinating agents, sulfuryl chloride, catalyzed as described, neither cleaves nor attacks the side chain. A practically quantitative yield of pentachlorotoluene may be obtained:
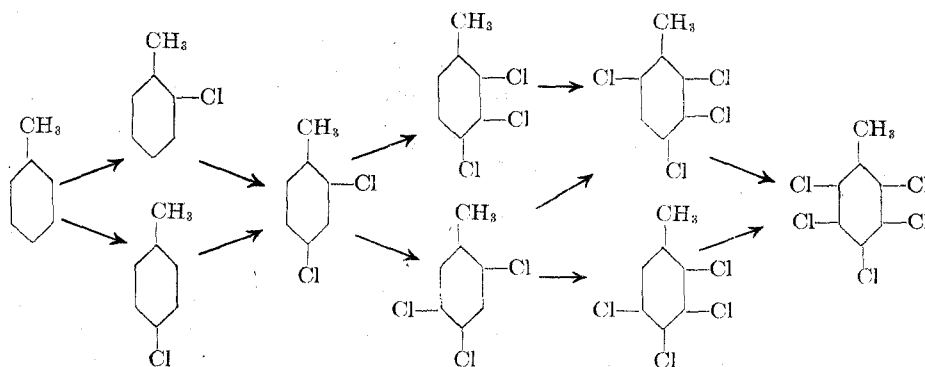
Silberrad also studied the effects of many substances on the ratio of nuclear and side-chain chlorination in toluene (*68*). The results are of doubtful value, however, because the toluene

he used probably contained peroxides (see "Chlorination of Aliphatic Compounds").

The sensitivity of sulfuryl chloride as a chlorinating agent to changes in the experimental conditions is well illustrated by its reported action on naphthalene. By slight alterations in the reaction conditions, naphthalene can be made to give 1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene, 1-chloronaphthalene, or 1,4-dichloronaphthalene (31, 60, 70):
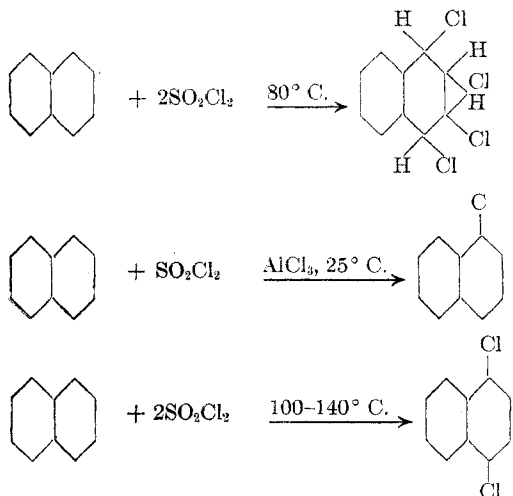

Many polynuclear hydrocarbons other than naphthalene may be chlorinated without the aid of catalysts. Under conditions similar to those used in the production of 1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene, pyrene yields chloropyrene and perylene yields a mixture of dichloro derivatives (60). At room temperatures anthracene is converted to the 9,10-dichloro derivative (5), whereas acenaphthene is substituted in the 3-position (20):
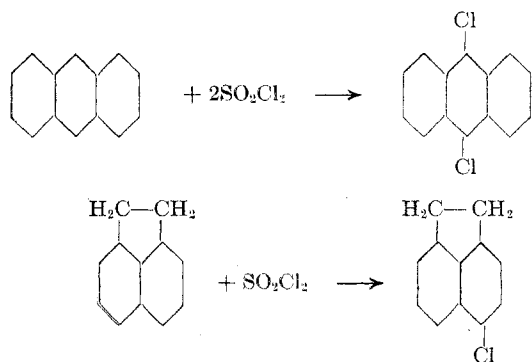
Heterocyclics are chlorinated under similar mild conditions. For example, indole has been converted into 2-chloroindole or into 2,3-dichloroindole, depending upon the quantity of sulfuryl chloride used (50); pyrazole at 0° C. yields 4-chloropyrazole (51); carbazole forms 3-chlorocarbazole (52). Although pyridine itself is not readily attacked, pyridine oxide reacts to give ultimately 2- and 4-chloropyridine (11).
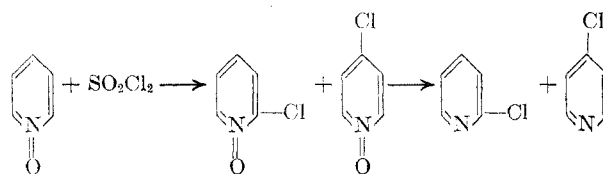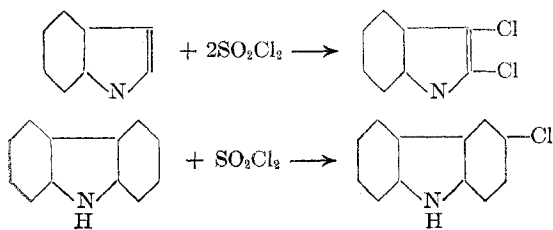

The chlorination of phenol and its derivatives has been a common application of sulfuryl chloride (3, 12, 23, 53, 57, 73). In general, the products obtained are the same as those produced by the action of gaseous chlorine; the reaction, however, is less vigorous and more easily controlled. Thus, the stepwise chlorination of resorcinol can be regulated to yield mono-, di-, or trichlororesorcinol as desired (62). Other examples of this application of sulfuryl chloride follow:
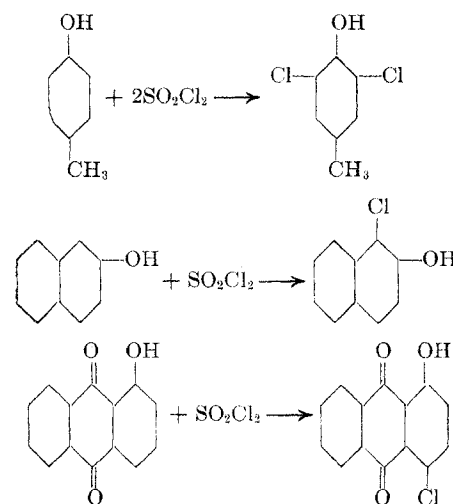

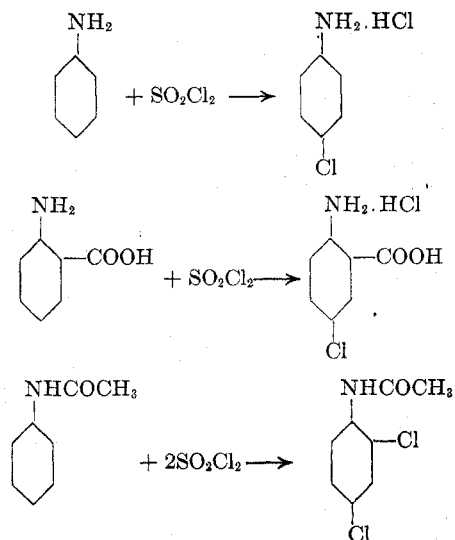In many instances practically quantitative yields are reported.

The use of sulfuryl chloride to prepare compounds of high germicidal properties by the chlorination of alkyl derivatives of cresol, resorcinol, and catechol is described in recent patents (45, 46, 55, 61):
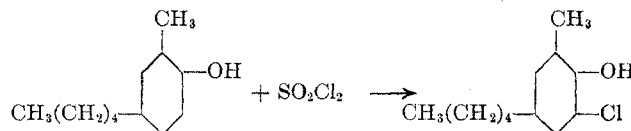
Phenol ethers are also chlorinated by sulfuryl chloride, although less readily than the phenols themselves (57). Phenol esters such as phenyl acetate or benzoate, triacetylphloroglucinol, etc., do not react under mild conditions in the absence of catalysts (57):
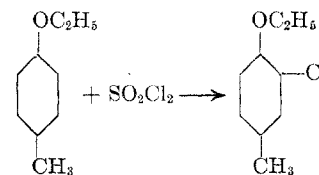
The reaction of aromatic amines and their derivatives with sulfuryl chloride has also received considerable attention. Aniline is readily chlorinated in the absence of catalysts to form the mono-, di-, and trichloro derivatives (25). Only three chlorine atoms can thus be introduced into the nucleus. Anthranilic acid is smoothly chlorinated to either a mono- or a dichloro derivative. Instead of the free amines, the acyl derivatives such as acetanilide may be used (25, 78):

NH$_2$ [benzene ring] + SO$_2$Cl$_2$ ⟶ NH$_2$·HCl [benzene ring with Cl]

NH$_2$ [benzene ring]—COOH + SO$_2$Cl$_2$ ⟶ NH$_2$·HCl [benzene ring]—COOH with Cl

NHCOCH$_3$ [benzene ring] + 2SO$_2$Cl$_2$ ⟶ NHCOCH$_3$ [benzene ring]—Cl with Cl

Several studies have recently appeared of the chlorination of aryl amides of aromatic acids by sulfuryl chloride (*32, 33*). The authors were interested in the effect of substituents in the basic and acidic parts of the molecule on the ease of halogenation. Although no detailed discussion of this work can be given here, one example will be presented. Benzanilide is readily chlorinated, first in the para position of the basic groups, then in the ortho position. However, the anilide of *o*-nitrobenzoic acid is much less reactive, and only one chlorine atom is introduced into the basic part of the molecule even under comparatively vigorous conditions:

HN—CO—[ring] ⟶ HN—CO—[ring] with Cl ⟶ HN—CO—[ring] with Cl and Cl

HN—CO—[ring]NO$_2$ ⟶ HN—CO—[ring]NO$_2$ with Cl
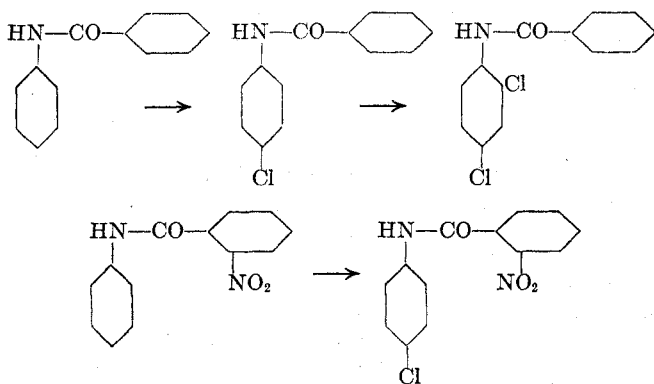
Except in a few instances, the action of sulfuryl chloride on aromatic aldehydes and ketones has not been studied. It is reported that benzophenone does not react with sulfuryl chloride in the absence of a catalyst, whereas benzaldehyde reacts to form benzoyl chloride rather than any nuclear chlorinated derivative (*24*).

The use of sulfuryl chloride as a solvent (as well as a chlorinating agent) for processes involving the chlorination and bromination of dyes and dye intermediates has been the subject of a number of patents (*15, 21, 44, 58, 75*). In certain instances, as in the chlorination and bromination of pyranthrone (*21*), the presence of the sulfuryl chloride appears to exert a directive influence on the reaction which is not shown by the other halogenating agents. This may be due to the reducing action of sulfur dioxide liberated during the reaction.

CHLORINATION OF ALIPHATIC COMPOUNDS

Until recently the only references to sulfuryl chloride as a chlorinating agent for a saturated aliphatic hydrocarbon were the patents covering the chlorination of methane at 300° C. in the presence of "ionizing" catalysts such as carbon (*13A, 49*). Under these vigorous conditions the sulfuryl chloride must be almost completely dissociated into sulfur dioxide and chlorine (*72*), and the chlorination of the hydrocarbon is probably due to the presence of free chlorine. On the other hand, the recently discovered chlorination of aliphatic hydrocarbons and their derivatives with sulfuryl chloride in the presence of small quantities of organic peroxides (*34, 35, 36, 38*) takes place at moderate temperatures. The mechanism of the reaction probably does not involve prior decomposition of sulfuryl chloride in the sense just mentioned.

In the absence of catalysts and light, sulfuryl chloride does not react with saturated aliphatic or alicyclic hydrocarbons such as *n*-heptane or cyclohexane at temperatures as high as the boiling points of the mixtures. Even in the presence of light, these hydrocarbons react only very slowly. Substances effective as catalysts in the chlorination of aromatic hydrocarbons here affect the rate of chlorination only slightly. In comparison, the effect of a trace of peroxide is striking: The addition of less than 1 mole % of benzoyl peroxide to the reaction mixture causes practically complete reaction in 30–60 minutes.

Study of the chlorination of various paraffin hydrocarbons and their halogen derivatives (*34*) indicates that, generally speaking, the products obtained by the use of sulfuryl chloride parallel those produced by the photochemical reaction with gaseous chlorine. Thus, the chlorination of *n*-heptane yields 15% of primary and 85% of secondary chlorides; 1-chlorobutane is substituted only slightly in the 1-position, 25% in the 2-, 50% in the 3-, and 25% in the 4-position. Neither chloroform nor *sym*-tetrachloroethane is further chlorinated by this method.

These and other similar results may be summarized in the following generalizations: (*a*) Substitution of hydrogen on a secondary carbon atom takes place in preference to substitution on a primary carbon atom; (*b*) a second substituent chlorine atom tends to attach itself to the aliphatic chain as far from the first chlorine atom as possible; (*c*) substitution of a second chlorine atom upon a carbon atom already bearing a halogen substituent is difficult, and a third chlorine atom cannot be attached to one carbon atom in this way.

The use of sulfuryl chloride as a chlorinating agent has hitherto been restricted primarily to aromatic nuclei in the presence of halogen carriers. However, the isolation of benzyl chloride from the chlorination product of toluene is reported in several instances. Dubois stated that toluene and sulfuryl chloride react slowly at 115° C. to form benzyl chloride and chlorotoluene (*22*), and Wohl patented the preparation of benzyl chloride by the action of sulfuryl chloride on toluene at 130° (*76*). Töhl and Eberhard stated that a refluxing mixture of toluene and sulfuryl chloride does not react (*70*); this statement has been questioned, and it has been claimed that toluene and sulfuryl chloride do react in the dark at reflux temperature (*68*).

It is now established that pure, peroxide-free toluene does not react at any appreciable rate with sulfuryl chloride in the dark even at the boiling point of the mixture (*34*). A small amount of added peroxide induces a vigorous reaction; nearly quantitative yields of benzyl chloride are obtained in a few minutes. In the presence of excess sulfuryl chloride the side chain is further chlorinated with the formation of benzal chloride. The introduction of a third chlorine atom into the side chain either does not take place or else occurs so slowly that, for practical purposes, the reaction may be neglected. This last observation supports the conclusion previously drawn from the inertness of *sym*-tetrachloroethane and chloroform: The accumulation of two chlorine atoms upon a carbon atom prevents further substitution (by this method of chlorination) upon that atom.

In general, derivatives and homologs of toluene readily undergo side-chain chlorination by sulfuryl chloride and peroxides; among the compounds investigated are *p*-chlorotoluene, ethyl-

benzene, and isopropylbenzene. o-Nitrotoluene and p-nitrotoluene, however, are exceptions; neither can be chlorinated by this method:
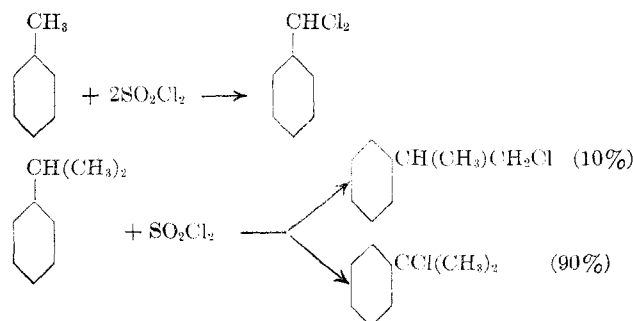
The peroxide–sulfuryl chloride method finds an especially useful application in the selective side-chain chlorination of aromatic hydrocarbons of moderately high nuclear reactivity. For example, it is stated that the photochemical chlorination of the side chain in m-xylene to form α-chloro-m-xylene is accompanied even under the most favorable conditions by the formation of at least 10% of 4-chloro-m-xylene (42). Chlorination of m-xylene with sulfuryl chloride and peroxides, however, yields pure α-chloro-m-xylene. It has also been reported that the side chain of tert-butylbenzene is so unreactive in the absence of peroxides that the side-chain halogen derivatives cannot be directly obtained; conditions under which reaction with halogens occurs lead only to nuclear-substituted products (64). However, in the presence of a peroxide, sulfuryl chloride chlorinates the side chain selectively and with ease. Unfortunately this type of selectivity is not universal. The nuclei of fluorene and β-methylnaphthalene, for example, are so reactive and nuclear substitution proceeds so readily, that the peroxide–sulfuryl chloride method cannot be used for the selective chlorination of the side chains of these compounds.

Sulfuryl chloride reacts readily with most alkenes to give the saturated dichloro derivatives and sulfur dioxide. This reaction is the subject of several patents. Among them are the formation of dichlorides from amylenes and hexenes by the reaction of sulfuryl chloride with the hydrocarbons below 30° C. (4) and the reaction of ethylene and propylene (in a mixture with saturated hydrocarbons) with sulfuryl chloride at 10–40° C. (14).

An investigation of the factors involved in the reaction has revealed that the chlorination is peroxide-catalyzed (35). Many unsaturated compounds (cyclohexene, allyl chloride) usually contain enough peroxidic material to permit the reaction to proceed easily without the addition of a peroxide catalyst. However, for the analogous chlorination of other, less oxygen-sensitive olefins (sym-dichloroethylene, stilbene), the addition of small quantities of peroxide is essential:
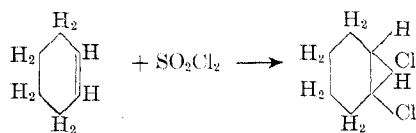

The chlorination of a simple acetylenic derivative with the reagent has not been described. It is claimed that divinylacetylene yields an oil which is probably 3,4-dichloro-1,3,5-hexatriene (18).
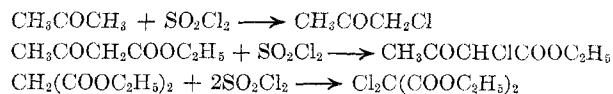
Sulfuryl chloride, together with peroxides, easily chlorinates aliphatic acids and acid chlorides (36). The hydrogen atoms in the α-position on the carbon chain are substituted with greater difficulty than those in the β- and γ-positions. That is, the product (except in the instance of acetic acid and acetyl chloride) consists chiefly of β- or of β- and γ-chlorinated acids, or the corresponding acid chlorides. For example, propionyl chloride

yields 40% α- and 60% β-chloropropionyl chloride, and n-butyryl chloride yields 15% α-, 55% β-, and 30% γ-chlorobutyryl chloride.

If, instead of peroxides, halogen carriers such as iodine are used to catalyze the reaction of sulfuryl chloride, substitution takes place only at the α-position. Hence, the mechanisms involved in catalysis by peroxides and by the usual type of halogen carriers must be of different types:
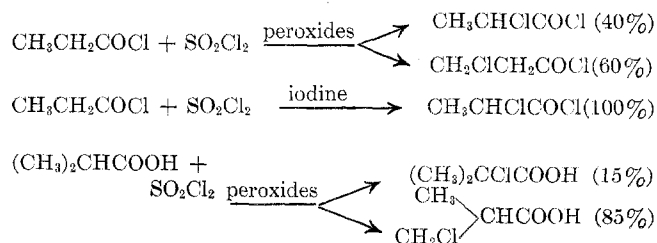
Aldehydes and ketones which do not contain an α-hydrogen atom undergo the usual peroxide-catalyzed reaction (40). Thus, benzaldehyde is converted by sulfuryl chloride to benzoyl chloride, and phenyl tert-butyl ketone is chlorinated in the alkyl group. Benzophenone does not react (24). If the compound contains an α-hydrogen atom, substitution in this position readily occurs at room temperature in the absence of added peroxide or other catalysts, probably by a mechanism involving the enol form of the compounds (2, 17, 48):

$$CH_3COCH_3 + SO_2Cl_2 \longrightarrow CH_3COCH_2Cl$$
$$CH_3COCH_2COOC_2H_5 + SO_2Cl_2 \longrightarrow CH_3COCHClCOOC_2H_5$$
$$CH_2(COOC_2H_5)_2 + 2SO_2Cl_2 \longrightarrow Cl_2C(COOC_2H_5)_2$$

The chlorination of γ-acetopropyl alcohol with sulfuryl chloride at 0° C. was recently patented as a means of preparing γ-chloro-γ-acetopropyl alcohol, an intermediate in the synthesis of vitamin B₁ (16, 59):

$$CH_3COCH_2CH_2CH_2OH + SO_2Cl_2 \longrightarrow$$
$$CH_3COCHClCH_2CH_2CH_2OH$$
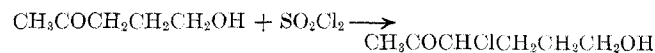
SULFONATION OF AROMATIC COMPOUNDS

The use of aluminum chloride with sulfur monochloride as a catalyst for the chlorination of aromatic compounds by sulfuryl chloride has already been discussed. Under slightly different conditions it is reported that aluminum chloride induces a different reaction—sulfonation of the aromatic nucleus. The procedure recommended by Töhl and Eberhard (70) is the addition of small quantities of the catalyst to a cooled reaction mixture of sulfuryl chloride and the hydrocarbon. By this method these authors prepared the sulfonyl chloride derivatives of many aromatic hydrocarbons, among them benzene, toluene, xylene, mesitylene, etc. The familiar orientation rules of oleum sulfonation are obeyed:
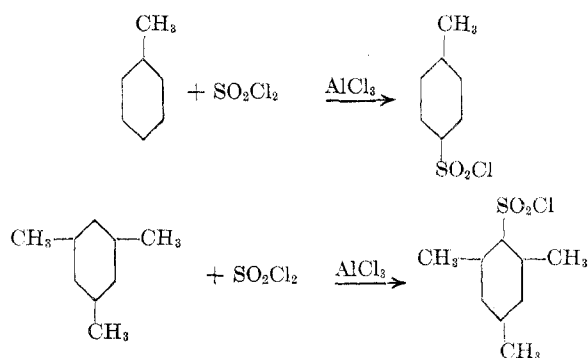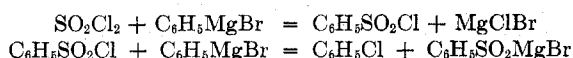

Besides the sulfonyl chloride derivatives which constitute the major part of the reaction product, relatively small quantities

of chlorinated hydrocarbons and sulfones are also formed. With the highly alkylated benzenes, such as durene and pentamethylbenzene, Töhl and Eberhard report that chlorination alone occurs.

Working at somewhat higher temperatures and using molar quantities of aluminum chloride, Böeseken observed that, in addition to sulfonyl chloride (13), sulfonic acids and large quantities of chlorinated derivatives are formed. Since he worked under conditions favorable to the dissociation of sulfuryl chloride, it is highly probable that the formation of these products is due not to the action of the reagent itself, but to the effect of its dissociation products, sulfur dioxide and chlorine.

Another method of introducing the sulfonyl chloride group into the aromatic nucleus may be mentioned, although its practical value in organic syntheses is uncertain. The reaction of the Grignard reagent with sulfuryl chloride takes place in two stages:

$$SO_2Cl_2 + C_6H_5MgBr = C_6H_5SO_2Cl + MgClBr$$
$$C_6H_5SO_2Cl + C_6H_5MgBr = C_6H_5Cl + C_6H_5SO_2MgBr$$

With the proper precautions it is possible to control the reaction so as to obtain fair yields of the sulfonyl chloride (19).
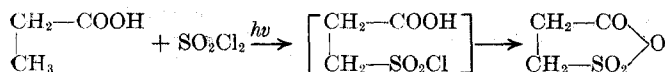
SULFONATION OF ALIPHATIC COMPOUNDS

Sulfuryl chloride also reacts with aliphatic Grignard reagents to form aliphatic sulfonyl chlorides (19). However, the yields are only moderate and the reaction has been but little used.

A better method of employing sulfuryl chloride to introduce the sulfonyl chloride group into aliphatic compounds has recently been developed (41). In the presence of light and a small quantity of suitable catalyst (e.g., pyridine or thiophenol) at 40–60°C., sulfuryl chloride and paraffin hydrocarbons undergo a rapid, vigorous reaction with the formation of alkyl sulfonyl chlorides. The yields are excellent, in some cases as high as 70%. Sulfonation is accompanied by the formation of smaller quantities of chlorinated products. Among the hydrocarbons which have been thus sulfonated are cyclohexane, n-butane, ethylbenzene, and tert-butylbenzene:
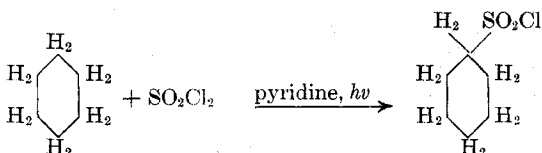

The reaction just mentioned has been extended to include other types of aliphatic compounds. In the treatment of the lower aliphatic acids (propionic, butyric, isobutyric) no catalyst need be added; the sulfonation proceeds rapidly and smoothly when a warm mixture of sulfuryl chloride and the organic acid is illuminated. The products isolated are not the sulfonyl chlorides, but a new class of compounds—the inner anhydrides of sulfocarboxylic acids (36, 39). These new substances should find valuable applications:


In the sulfonation of the higher aliphatic acids (lauric, palmitic) the addition of a small quantity of pyridine or some similar catalyst is required for optimum results. A large proportion of the substitution must occur in positions unfavorable to cyclization, since the products isolated consist primarily of the sulfonyl chlorides.
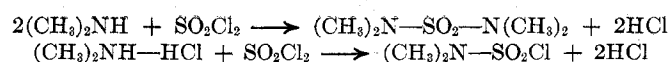
REACTIONS AS AN ACYL DERIVATIVE

In many reactions sulfuryl chloride reacts as an acid chloride of sulfuric acid. For example, with many aliphatic alcohols it forms the alkyl chlorosulfonates (8, 10). Under proper conditions good yields can be obtained:

$$CH_3CH_2CH_2OH + SO_2Cl_2 = CH_3CH_2CH_2OSO_2Cl + HCl$$
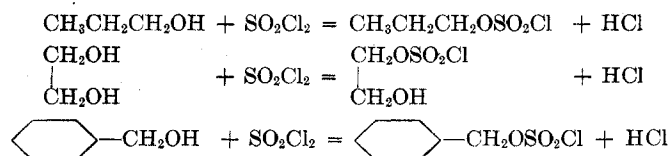
With an excess of alcohol, the reaction may proceed to the formation of (a) dialkyl sulfate or (b) alkyl sulfuric acid (47):

(a) $CH_3OSO_2Cl + CH_3OH = (CH_3)_2SO_4 + HCl$
(b) $CH_3OSO_2Cl + CH_3OH = CH_3OSO_3H + CH_3Cl$
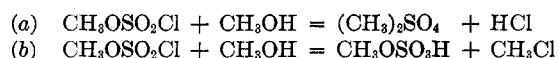
Aliphatic amines undergo similar reactions. Secondary amines such as dimethylamine or piperidine form the symmetrical sulfamide derivatives unless special precautions are taken (9, 10, 71). The hydrochlorides of these amines react less vigorously, and the reaction stops after the combination of a molecule of sulfuryl chloride with one molecule of the amine hydrochloride:

$$2(CH_3)_2NH + SO_2Cl_2 \longrightarrow (CH_3)_2N-SO_2-N(CH_3)_2 + 2HCl$$
$$(CH_3)_2NH-HCl + SO_2Cl_2 \longrightarrow (CH_3)_2N-SO_2Cl + 2HCl$$
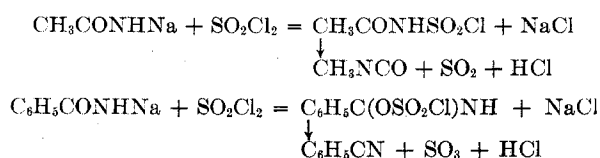
Although practically all the work on this reaction has dealt with secondary amines, one primary aliphatic amine is known to react in the same way (27).

Under the proper conditions, sulfuryl chloride reacts primarily as an acylating agent, even with aromatic amines. Thus, Wohl and Koch reported that a 60% yield of sulfanilide is obtained by dropping sulfuryl chloride dissolved in dry ether into a cooled solution of aniline dissolved in about three times its volume of dry ether. Azobenzene is formed as a by-product. p-Toluidine undergoes a similar reaction (77).

Although acyl derivatives of the aromatic amines do not take part in a reaction analogous to those just mentioned, the metal derivatives of the aryl amides and sulfonamides have been found to react (54):
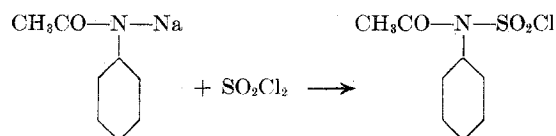
The metal derivatives of the unsubstituted amides do not yield stable chlorosulfonyl derivatives when treated with sulfuryl chloride. Two typical reactions (6) are:

$$CH_3CONHNa + SO_2Cl_2 = CH_3CONHSO_2Cl + NaCl$$
$$\downarrow$$
$$CH_3NCO + SO_2 + HCl$$

$$C_6H_5CONHNa + SO_2Cl_2 = C_6H_5C(OSO_2Cl)NH + NaCl$$
$$\downarrow$$
$$C_6H_5CN + SO_3 + HCl$$

An interesting use of sulfuryl chloride in acylation reactions was reported by Baumgarten (7). The addition compound of sulfuryl chloride with pyridine, dissolved in an excess of pyridine, reacts with alcohols and acids to form the alkyl and acyl chlorides, respectively. If a phenol or an amine is present, it is acylated:
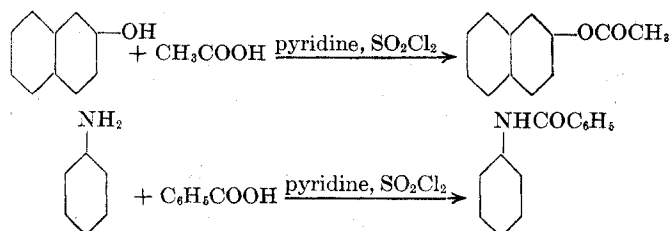

By the action of sulfuryl chloride on the sodium salts of organic acids, acid chlorides and acid anhydrides are formed. Ben-

zoyl chloride and benzoic anhydride have been made in this way from sodium benzoate (43), and the corresponding phenylacetyl derivatives have been similarly prepared from sodium phenyl acetate (24).

The application of the same reaction to the manufacture of acetic anhydride has received considerable attention (30). Methods are described involving the action of sulfuryl chloride on sodium and calcium acetates in varying proportions to yield either the acid chloride or the acid anhydride (74). In one ingenious process, sulfur dioxide and chlorine are passed into acetic anhydride, which catalyzes the formation of sulfuryl chloride, and the mixture is then run onto anhydrous sodium acetate. After completion of the reaction, the acetic anhydride is recovered by distillation (1).

MISCELLANEOUS APPLICATIONS

The treatment of β-naphthylamine with sulfuryl chloride in the presence of pyridine, followed by addition of calcium oxide and sublimation of the product, leads to a 98% yield of α,β-naphthazine (63):
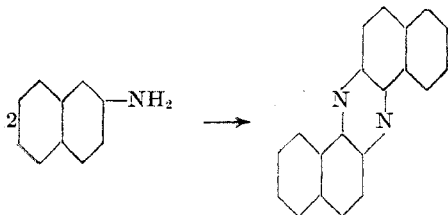

The nature of the products obtained by the analogous treatment of α-naphthylamine and benzidine has not yet been elucidated.

Treatment of α-trioxymethylene with sulfuryl chloride gives chloroacetic acid in good yield (29).

Sulfuryl chloride catalyzes the polymerization of cyclopentadiene to "cyclopentadiene rubber" (69).

It is claimed that good yields of a $C_{12}H_{22}$ hydrocarbon (probably dimethyldicyclopentyl) are obtained by the action of sulfuryl chloride on cyclohexane in the presence of aluminum chloride (56).

Recently Friese and Djiang (28) reported that in the presence of a mixture of acetic acid and acetic anhydride, sulfuryl chloride reacts with cyclohexene to form the acetyl ester of cyclohexene chlorohydrin:
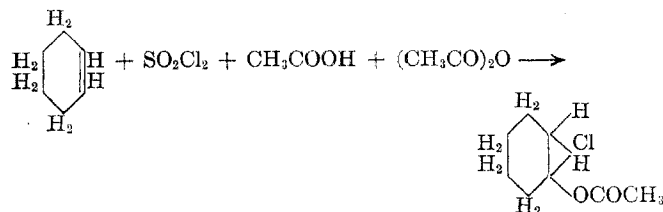
Neither sulfuryl chloride and acetic acid nor sulfuryl chloride and acetic anhydride are capable of inducing the reaction. All three of the components (sulfuryl chloride, acetic acid, and acetic anhydride) are necessary.

The use of sulfuryl chloride as an antishrink agent for wool may be mentioned. This process has received considerable attention and recently Elliot and Speakman (26) sought an explanation for this property of sulfuryl chloride.

THEORETICAL IMPLICATIONS

The study of sulfuryl chloride reactions has not yielded results of interest only to the practical chemist, as the discussion might seem to indicate. Far-reaching in its implications to theoretical organic chemistry is the light which has been cast on the relation between "reactivity" and "mechanism". To mention one example, aromatic hydrocarbons (benzene, toluene), which are ordinarily considered "reactive" hydrocarbons, do not react with sulfuryl chloride in the presence of peroxides; the so-called unreactive paraffin hydrocarbons react under these conditions with marked ease; with halogen carriers (such as iodine, sulfur, etc.) the reverse phenomenon is observed. Moreover, the reactive benzenoid hydrocarbons do not take part in the photochemical and sulfonation reaction with sulfuryl chloride in which the aliphatic hydrocarbons so readily participate; on the other hand, the aliphatic hydrocarbons are not affected by the conditions (aluminum chloride and sulfuryl chloride) which so readily lead to the sulfonation of aromatic hydrocarbons.

These anomalies are readily explained once the assumption is made that aromatic hydrocarbons react primarily by an ionic or polar type mechanism, whereas paraffin hydrocarbons react by a mechanism involving atoms or free radicals (34, 36, 39). This interpretation not only clarifies the points just raised, but indicates the directions in which the search for new low-temperature reactions of the paraffin hydrocarbons should proceed (37).

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Vulcanization of GR-I

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The most rapid sulfur vulcanization of GR-I requires the use of ultra-accelerators. Increase of accelerator concentration above certain points produces inferior original physical properties with no advantage in cure rate. An excess of zinc oxide over that necessary to obtain maximum tensile is required to produce the maximum in modulus and vulcanizate stability. For low-temperature curing the metal salt accelerators should be used, alone or in conjunction with other accelerators to obtain fast cure rate. Reversion is apparent in GR-I vulcanizates if curing times are long enough or temperatures are high enough. Decreasing the rate of vulcanization with less active accelerators delays appearance of the reversion phenomenon.

THE early recognition by the rubber industry of the relatively low cure rate of sulfur-vulcanized Butyl rubber and its effect on factory production led to considerable work on means of increasing the cure rate. One obvious method is to introduce more unsaturation into the polymer; but even though the cure rate of GR-I has been improved over that of the early Butyl (*11*), it is still considered a slow-curing polymer. With a realization of the limitations imposed upon GR-I because of its inability to fit into production schedules designed around the use of natural rubber, this study presents some important aspects of the sulfur vulcanization of GR-I. Ever since the discovery and development of organic accelerators, the search has been continued for a simple method of relating physical properties to cure state. Early attempts to relate combined sulfur to physical properties had little significance (*5, 10*). Recently (*9*) methods for isolating definite forms of combined sulfur have been developed, and it is possible that these may lead to better relations between chemically combined sulfur of a definite type and physical properties.

Many physical tests have been utilized to determine state of cure. By a statistical treatment of cross-linked polymers (*4*) it is possible to relate rubberlike elasticity and swelling capacity to concentration of cross links. Of these relations, the property of rubberlike elasticity in a modified form is the most
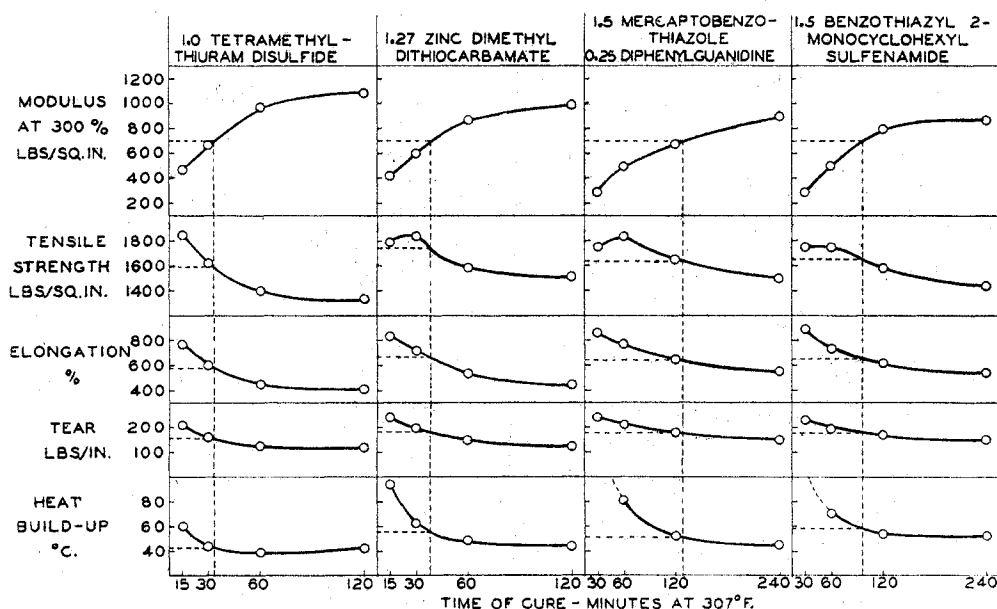

Figure 1. Effect of Accelerator Type on GR-I Vulcanization