PROOF OF STRUCTURE OF SOME CONTROVERSIAL SULFONYL CHLORIDES

by

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INTRODUCTION

A comprehensive investigation of reaction mechanisms of sulfonyl compounds was initiated in this Laboratory in 1949. At that time an insight into these reaction mechanisms was sought by determining the steric requirements of several branched chain sulfonyl chlorides so that they could be compared with analogously branched primary alkyl halides in order to test the assumption that the sulfonyl group acts as a pseudo-methylene group. In the course of the investigation the study has been broadened to include other types of sulfonyl compounds; namely, polyfunctional sulfonyl chlorides, sulfonic acid esters, and sultones.

It has been claimed that photochemical chlorosulfonylations of isopentyl chloride and 4-methyl-2-pentyl chloride produce the corresponding chloro tertiary sulfonyl chlorides[1] but evidence

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[1] H. Helberger, G. Manecke, and H. Fischer, Ann., 562, 23 (1949).

developed in this Laboratory[1] and elsewhere[2] has almost conclusively proved that the sulfonyl chlorides are primary ones. The most convincing proof would be to convert the sulfonyl chlorides into substances of known structure. It was the purpose of this investigation to so prove the structures of these sulfonyl chlorides. It was decided to accomplish this proof by isolation of the sulfonyl chlorides (showing absence of isomeric products), conversion of these to the sultones (structures of which have been proved), and also reduction of the sulfonyl chlorides to the oorresponding unsubstituted mercaptans, with unequivocal syntheses of these mercaptans. As it is customary to establish identity of a liquid product with a solid derivative, it was decided to prepare such derivatives of each sulfonyl chloride and mercaptan.

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[1] M. K. Frye, M. S. Thesis, 1951, University of Alabama, University, Alabama, and M. S. Heller, PhD Dissertation, 1955, University of Alabama, University, Alabama.

[2] F. Asinger and F. Ebeneder, Ber., 75, 344 (1942), and F. Asinger, G. Geiseler, and M. Hoppe, Ber., 91, 2130 (1953).

THE PHOTOCHEMICAL CHLOROSULFONYLATION OF ALKANES

The conversion of alkanes to the corresponding alkanesulfonyl chlorides by the photochemical reaction of sulfur dioxide and chlorine with paraffin hydrocarbons (the Reed reaction[1]) is represented by the over-all equation:

$$R\text{-}H + SO_2 + Cl_2 \xrightarrow{h\nu} RSO_2Cl + HCl.$$

Due to the unshared pair of valence electrons about the sulfur atom in sulfur dioxide, this compound may enter into the chain reaction which occurs during photochemical chlorination of hydrocarbons. Thus, with the conjoint action of sulfur dioxide and chlorine gases on saturated hydrocarbons in the liquid phase under strong illumination with short wave length visible or ultraviolet light sulfonyl chlorides are obtained. The products, in addition to sulfonyl chlorides, usually include some chloroalkanes and polysulfonated material,[2] higher temperatures favoring chlorination. The reaction mechanism has been thoroughly studied and seems to indicate the following

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[1] C. F. Reed, U. S. Patent, 2,046,090 (June 13, 1936); Ref. cit., C. A., 30, 5593 (1936).

[2] C. Walling, "Free Radicals in Solution" (John Wiley and Sons, Inc., New York, 1957), p. 394.

steps:[1,2,3,4]

$$Cl_2 + h\nu \longrightarrow 2Cl\cdot$$

$$R\text{-}H + Cl\cdot \longrightarrow R\cdot + HCl$$

$$R\cdot + SO_2 \rightleftharpoons RSO_2\cdot$$

$$R\cdot + Cl\text{-}Cl \longrightarrow RCl + Cl\cdot$$

$$RSO_2\cdot + Cl\text{-}Cl \longrightarrow RSO_2Cl + Cl\cdot$$

The quantum yield (3000-5000 Å) is about 2000. The usual procedure for carrying out the reaction is to pass a mixture of chlorine and an excess of sulfur dioxide into an irradiated liquid phase of the hydrocarbon, with or without a suitable diluent such as carbon tetrachloride, at about 10-30°. In this study the diluent was omitted. The reason for this was that neither Asinger nor Helberger mentioned a solvent. As one phase of the problem was to attempt to duplicate their yields, none was used.

When a straight chain hydrocarbon is subjected to the abovementioned Reed reaction, the only sulfonyl chlorides obtained are

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[1] F. Povenz, Z. Elektrochem., 56, 746 (1952).

[2] J. Stauff, ibid., 49, 550 (1942).

[3] P. Herold, Reichsamt Wirschaftsausbau, Prüf - Nr. 102, (PB 52004), 69-74 (1940), C. A., 41, 6527 (1947).

[4] H. Helberger, Angew. Chem., 55, 172 (1942).

primary and secondary ones.[1] If the hydrocarbon contains tertiary hydrogen atoms there might be the theoretical possiblity of forming tertiary sulfonyl chlorides, for the tertiary hydrogen atom is the most susceptible and the primary least to analogous chlorinations. However, the tertiary sulfonyl chloride is very unstable for two reasons; (1) the inductive effective of the side-chain weakens both the carbon-sulfur and the sulfur-chlorine bond, and (2) the backstrain ("B"-strain) makes the compound less stable.

Asinger[2] claims to have prepared t-isobutanesulfonyl chloride by reacting the sodium salt of the corresponding sulfonic acid with phosphorus pentachloride. Unfortunately, a detailed description of experimental conditions was omitted in the publication. The product obtained is reported to be a stable liquid boiling at 80°/15 mm, which readily reacts "normally" with cyclohexylamine to give a solid derivative melting at 61.5°. Frye,[3] in this Laboratory and Hunt,[4] with duPont, were unsuccessful in duplicating Asinger's work. However, Frye did prepare t-isobutanesulfonyl chloride by reacting t-butylmagnesium chloride with sulfuryl chloride. This sulfonyl

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[1] F. Asinger, W. Schmidt, and F. Ebeneder, ibid., 75, 34 (1942).

[2] F. Asinger and F. Ebeneder, ibid., 75, 344 (1942).

[3] M. K. Frye, op. cit.

[4] See Appendix.

chloride melts at 89-91° as would be expected from its symmetrical structure. A solid derivative of the sulfonyl chloride could not be prepared in this Laboratory, indicating great steric hindrance to such a reaction.

The t-isobutanesulfonyl chloride prepared by Frye rapidly decomposes into t-butyl chloride and sulfur dioxide by first order kinetics. It has a half-life of 240, 34, and 6 hours at 25°, 35°, and 50°, respectively.[1] This is in accord with the belief that the simple tertiary sufonyl chlorides should be relatively unstable ("B"-strain).

From this and other investigations conducted recently in this Laboratory it is believed that the compound prepared by Asinger is not a sulfonyl chloride.

Photochemical chlorosulfonylation is applicable to all saturated alkanes above methane in the liquid phase; however, only a few of these give individual sulfonyl chlorides that can readily be isolated. Low molecular weight paraffins such as propane and butane yield mixtures of primary and secondary products which are easily separated.[2,3,4,5,6] Some branched chain paraffins such as

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[1] Frye, op. cit.

[2] F. Asinger, W. Schmidt, and F. Ebeneder, loc. cit.

[3] F. Asinger, F. Ebeneder, and E. Bock, ibid., 75, 42 (1942).

[4] F. Asinger and F. Ebeneder, ibid., 75, 344 (1942).

[5] H. Helberger, G. Manecke, and H. Fisher, loc. cit.

[6] A. P. Terent'ov and A. I. Gershenovich, Zhur. Obshchei Khim., 23, 204 (1953).

isobutane[1], 2, 3-dimethylbutane and neopentane[3] give only one monosubstituted products. This is also true of alicyclic alkanes such as cyclopentane[4] and cyclohexane.[5] When long chain hydrocarbons are used a mixture of products is necessarily produced and separation of isomers is usually very difficult and impracticable. Chlorosulfonylation of such hydrocarbons takes place in a largely statistical manner[6] as in the case of chlorination. When polysulfonylation occurs, the substituted positions are at least three carbon atoms apart.

According to Lockwood[7] when 10 to 20 per cent of the usual alkane is chlorosulfonylated, about 90 per cent of the sulfonation product is mono- and 10 per cent disulfonyl chlorides. At 50 per cent conversion, approximately 70 per cent is monosulfonyl chlorides, while with 70 per cent conversion about equal amounts of mono- and disulfonyl chlorides are formed. From these data, the optimum conversion to the monosulfonyl chlorides is around 60 per

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[1] F. Asinger and F. Ebeneder, loc. cit.

[2] R. B. Scott and M. S. Heller, J. Org. Chem., 20, 1159 (1955).

[3] R. B. Scott and H. L. McLeod, J. Org. Chem., 21, 388 (1956).

[4] J. P. Stutts, M. S. Thesis, 1954, University of Alabama, University, Alabama.

[5] A. L. Fox, U. S Patent, 2,174,509 (Sept. 26, 1939); Ref. cit. W. H. Lockwood Chem. Ind., 62-63, 760 (1948).

[6] Lockwood, ibid.

[7] Lockwood, ibid.

cent if the unreacted hydrocarbon is not to be recovered.

Substantially the same photochemical chlorosulfonylation has been developed by Kharasch and Read[1] using sulfuryl chloride rather than a mixture of sulfur dioxide and chlorine. In this case the presence of a catalyst, such as pyridine, quinoline, or stearamide[2] is necessary to break down the sulfuryl chloride into sulfur dioxide and chloride, otherwise exclusively chlorination of the alkane occurs. Since it also is necessary to reflux the sulfuryl chloride (79°) considerably more chlorination occurs than in the usual Reed reaction.

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[1] M. S. Kharasch and A. T. Read, J. Am. Chem. Soc., 61, 3089 (1939).

[2] Lockwood, loc. cit.

TERTIARY SULFONYL CHLORIDES

During the past ten years emphasis has been placed on study of tertiary sulfonyl chlorides in this Laboratory. This is due to the fact that certain discrepancies regarding them have appeared in the literature. The following section is a general review of tertiary sulfonyl chlorides.

Synthesis of Tertiary Sulfonyl Chlorides

There are five different routes for the preparation of aliphatic sulfonyl chlorides: (1) the reaction between sulfonic acids or their salts and acid chlorides (phosphorus chlorides, thionyl chloride, phosgene); (2) oxidation of aliphatic sulfur bodies with chlorine in aqueous media;[1] (3) chlorination of sulfinic acids or their salts;[2] (4) treatment of Grignard reagents with sulfuryl chloride;[3] (5) photochemical chlorosulfonylation of

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[1] T. B. Johnson and J. M. Sprague, J. Am. Chem. Soc., 58, 1348 (1936).

[2] W. Borsche and W. Lange, Ber. 38, 2766 (1905); 39, 392 (1906); 40, 2220 (1907).

[3] E. Cherbuliez and O. Schnauder, Helv. Chim. Acta, 6, 249 (1923).

paraffinic hydrocarbons.[1]

All of these methods are adequate for the preparation of primary and secondary sulfonyl chlorides, but the reported data on tertiary sulfonyl compounds are meager and conflicting. One may conclude, from the information presented earlier that only reaction of a Grignard reagent with sulfuryl chloride or chlorination of a sulfinic acid salt appear likely methods for the formation of a tertiary sulfonyl chloride.

The synthesis of sulfonyl halides via sulfuryl chloride and the Grignard reagent has been shown to pass through a chloromagnesium salt of the sulfinic acid (RSO_2MgCl).[2] Salts produced from saturated Grignard compounds normally are not subject to molecular rearrangements. Further, if one considers the sulfinyl group as a pseudo-methylene group, the salts are somewhat analogous to Grignard reagents. It is known that chlorination of a Grignard compound yields the corresponding alkyl chloride. Therefore, one might expect to obtain a sulfonyl chloride from chloromagnesium sulfinates.

When acid chlorides and sulfonic acids (or their salts) are

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[1] Reed, loc. cit.

[2] R. B. Scott, J. B. Gayle, M. S. Heller, and R. E. Lutz, J. Org. Chem., 20, 1165 (1955).

used for the production of sulfonyl chlorides the intermediates, as RSO_2-O-SO-Cl, may be formed possibly, as in formation of alkyl chlorides by the action of thionyl chloride on alcohols. Decomposition of this intermediate to the sulfonyl compound would follow one of three routes, i.e., S_N1, S_N2, and S_Ni. Most likely the reaction proceeds by a bimolecular attack (S_N2) at the rear face of the sulfur atom. This is quite satisfactory for relatively unhindered sulfonic acids, however, because of great steric hindrance to such attack, a tertiary sulfonic acid might be forced through the unimolecular reaction (S_N1). A probable intermediate, therefore, is a sulfonylium ion (RSO_2^+) which, unlike a carbonium ion, could decompose to give sulfur dioxide and a carbonium ion ,leading to either an alkyl chloride or an olefin. Thus, a tertiary sulfonyl chloride is not likely product by this method.

When sulfonyl chlorides are prepared by the oxidative chlorination of various sulfur bodies, yields are good if the sulfur is attached to a primary carbon but only fair if attached to a secondary one. Further, Sprague and Johnson[1] have shown that no sulfonyl chloride is obtained when the sulfur atom is joined to tertiary carbon; the sulfur being oxidized completely to sulfuric acid.

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[1] J. M. Sprague and T. B. Johnson, J. Am. Chem. Soc., 59, 1837 (1937).

Helberger et al.[1] claim to have synthesized the tertiary sulfonyl chloride of isoamyl chloride through the Reed reaction. This is in marked disagreement with Asinger[2] and Scott[3] who showed that a tertiary sulfonyl compound is not formed from isobutane and 2,3-dimethylbutane, respectively. Asinger reasoned that there is too much hindrance at the tertiary carbon for an attack forming a relatively large sulfonyl free radical. While photochemical chlorination favors formation of tertiary chlorides, particularly at a low temperature, chlorosulfonylation does not, undoubtedly because the steric factor just mentioned would lead to an unstable sulfonyl free radical in equilibrium with the more stable tertiary free radical. It is doubtful that any sulfonyl chloride is formed, and, if any were, it would decompose in short order.[4]

Consequently, it is believed that only reaction of a Grignard reagent with sulfuryl chloride or chlorination of a sulfinic acid salt appear likely methods for the formation of a tertiary sulfonyl chloride.

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[1] J. Helberger, G. Manecke, and H. Fischer, loc. cit.

[2] F. Asinger and F. Ebeneder, loc. cit.

[3] Scott and Heller, loc. cit.

[4] M. K. Frye, op. cit.

DECOMPOSITION OF SULFONYL CHLORIDES

It is generally accepted that the thermal stability of aliphatic sulfonyl chlorides decreases in the following order: primary > secondary > tertiary. Probably only the primary compound is stable at room temperature, some secondary, and probably all tertiary ones deoompose on standing. Of course, almost all of the low molecular weight aliphatic sulfonyl chlorides decompose in the presence of ultraviolet light.[1]

The thermal decomposition of sulfonyl chlorides appears to be autocatalytic. Instead of homolysis, this decomposition may involve an S_N1 type reaction (ionization) to the sulfonylium ion which forms a carbonium ion on loss of sulfur dioxide. Lewis acids are known to catalyze decomposition;[2] possible mechanism for this is shown by the following scheme:

$$RSO_2Cl + AlCl_3 \longrightarrow RSO_2^+ + AlCl_4^-$$

$$RSO_2^+ \longrightarrow R^+ + SO_2$$

$$R^+ + AlCl_4^- \longrightarrow RCl + AlCl_3$$

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[1] M. A. Smook, E. T. Pieski, and C. F. Hammer, *Ind. Eng. Chem.*, *45*, 2731 (1953).

[2] R. B. Scott, Jr., PhD. Dissertation, 1949, University of Virginia, Charlottesville, Virginia.

It, therefore, seems quite likely that if this decomposition were controlled under the proper conditions this might be another proof of structure technique, provided carbonium ion rearrangement does not intrude. Thus, if a primary chloride is obtained, the sulfonyl chloride most certainly was primary. Terent'ev[1] has demonstrated the possibility of some relatively simple sulfonyl chlorides decomposing to the corresponding chlorides, however, primary isobutane represented the most severe test.

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[1] Terent'ev and Gershenovich, loc. cit.

CONCERNING A CLAIM AND A COUNTER-CLAIM TO PREPARING TERTIARY SULFONYL CHLORIDES PHOTOCHEMICALLY

As mentioned earlier, tertiary sulfonyl chlorides should be highly unstable and non-obtainable through chlorosulfonylation. However, Helberger _et al._[1] claim to have prepared and isolated several tertiary sulfonyl chlorides by the Reed reaction. Helberger seemed to disregard the published data of Asinger and Ebeneder[2] that the tertiary sulfonyl chloride of isobutane is not obtained. Later Scott[3] showed that no tertiary sulfonyl chloride of 2,3-dimethylbutane is formed. It therefore seems doubtful that Helberger actually obtained a tertiary sulfonyl compound. On examination of the article by Helberger one finds no proof of structure offered, and the reasoning presented for his conclusions are unfounded.

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[1] Helberger, Manecke, and Fisher, _loc. cit._

[2] Asinger and Ebeneder, _loc. cit._

[3] Scott and Heller, _loc. cit._

Recently, Heller[1] and Asinger,[2] in working with sultones, which result from intramolecular dehydrochlorination of the chloro-sulfonic acids or dehydration of the corresponding hydroxy-sulfonic acids obtained on hydroloysis of certain chloro-sulfonyl chlorides, showed that the sulfonyl chlorides must have been primary. Unfortunately, Heller did not isolate his sulfonyl chloride and the yields of sultones were low, therefore leaving the unlikely possibility that the tertiary sulfonyl chlorides also were present and the corresponding sultones lost in handling.

It must be noted that the cyclization step itself is not free from possible rearrangement, thus Truce[3] found that 5-hydroxy-1-pentanesulfonic acid is dehydrated to the sultone of the 4-hydroxy isomer. However, the question under study involves the sulfonic carbon, not the chloro or hydroxy carbon.

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[1] M. S. Heller, PhD. Dissertation, 1955, University of Alabama, University, Alabama.

[2] Asinger, Geiseler and Hoppe, loc. cit.

[3] W. E. Truce and F. D. Hoerger, J. Am. Chem. Soc., 76, 5357 (1954).

EXPERIMENTAL

4-Chloro-2-methyl-1-butanesulfonyl Chloride from 4-Chloro-2-Methylbutane

Two moles (236 ml, 210 g) of isopentyl chloride n_D^{20} 1.4095, (Columbia Organic Chemical Co.) was placed in a round-bottom flask fitted with a cork stopper holding a gas inlet tube, reflux condenser, thermometer, and stirrer. A mixture of gases was introduced at a rate of 4.5 liters of sulfur dioxide and 3 liters of chlorine per hour into the isopentyl chloride which was irradiated by 150-watt General Electric Par 38 Projector Flood lamp for 17 hours. Considerable heat was evolved but the temperature was kept at 15° - 25° by cooling with an ice-water bath. The reaction mixture was washed with three 100-ml portions of water, three 300-ml portions of 5% sodium bisulfite, and again with water. The crude sulfonyl chloride was dried over anhydrous magnesium sulfate for 12 hours. The product then was vacuum distilled through a modified Claisen flask, b. p. 139° - 141°/15 mm, n_D^{20} 1.4906, d_4^{20} 1.3432, M_D 44.2 (theory 44.5). A yield of 37.0 g (0.18 mole, 9% conversion based on alkyl chloride used) was obtained. While this conversion was low, compared to the 48.1% reported by Asinger,[1] there was no appreciable decomposition of sulfonyl chloride during distillation; thereby obviating the possibility of a large amount

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[1] F. Asinger and G. Geiseler, and M. Hoppe, loc. cit.

of an unstable sulfonyl chloride being lost. It is entire possible that the amount of chlorine used is in error as it was based upon flowmeter readings, the cylinder of chlorine being too large for accurately weighing. Asinger[1] and Helberger[2] reported only the boiling point, (139° - 141°/15 mm). Asinger gives an analysis of the compound and claims a 48.1% yield. Infrared data show characteristic sulfonyl chloride absorption bands[3] at 1175 (8.50μ) and 1375 (7.30μ) cm^{-1}.

Preparation of 4-Hydroxy-2-methyl-1-butane sulfonic Acid Sultone

4-Hydroxy-2-methyl-1-butanesulfonic acid sultone was prepared according to Asinger *et al.*[4] Thus,10 g of the chloroisopentanesulfonyl chloride obtained by chlorosulfonylation was heated for 5 hours with 25-ml of water under reflux. The chloroisopentanesulfonic acid and any hydroxy analog remained as a brown syrupy liquid after distilling off the water. The acid then was heated under 15 mm at 230°, after a short period of hydrogen chloride evolution the crude sultone distilled over as a colored liquid at 151° - 157°. The material was taken up in 50-ml

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[1] F. Asinger and G. Geiseler, and M. Hoppe, *ibid*.

[2] H. Helberger, G. Manecke, and H. Fischer, *Ann.*, *562*, 23 (1949).

[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules" (John Wiley and Sons, Inc., New York, 1959) second edition, pp. 363-366.

[4] Asinger, Geiseler, and Hoppe, *loc. cit.*

of ether and washed with 30 ml of water, 30 ml of 5% aqueous sodium bicarbonate, and again with water. The sultone-ether mixture was quickly dried with calcium chloride, then shaken with anhydrous magnesium sulfate overnight. The residue from removal of the ether was distilled in a modified Claisen flask to yield 2.0 g (28%) of a slightly tan colored 4-hydroxy-2-methyl-1-butanesulfonic acid sultone. The physical properties are: b.p. 151° - 153°/15 mm and n_D^{20} 1.4613[1] in agreement with Helberger.[2] Infrared data show characteristic bands[3] at 1175 (8.55μ), 1270 (7.86μ), and 1370 (7.32μ) cm^{-1}.[4]

Conversion of 4-Chloro-2-methyl-1-butanesulfonyl Chloride to 2-Methyl-1-butanethiol

The chloroisopentanesulfonyl chloride was reduced with lithium aluminum hydride as described by Brown.[5]

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[1] Asinger reported b.p. of 123° - 125°/3 mm and n_D^{20} 1.4612.

[2] Helberger, Manecke, and Fischer, loc. cit.

[3] L. J. Bellamy, op. cit.

[4] Bands agree with those reported by Asinger.

[5] H. G. Brown, "Organic Reactions" (John Wiley and Sons, Inc., New York, 1951), vol. 6, pp. 469-493.

The apparatus consisted of a stoppered one-liter three-necked flask provided with a magnetic stirrer, dropping funnel, reflux condenser and thermometer. Normal precautions were taken to ensure that the apparatus was dry, and the opening in the reflux condenser was fitted with a calcium chloride drying tube. The reduction was conducted under the hood as follows: A 0.5 molar stock solution (300 ml, 0.5 mole) of lithium aluminum hydride in ether was transferred to the reaction flask. A solution of 20.5 g (0.1 mole) of the sulfonyl chloride in 143 ml (100 g) of dry ether was added to the vigorously stirred solution from the dropping funnel at such a rate that the temperature did not rise above 30°. The addition required 4 hours. The mixture was stirred overnight. Water then was placed in the dropping funnel, and, with an ice bath surrounding the reaction container, was added dropwise until there was no evidence of further hydrogen gas evolution. Then 250 ml of 10% sulfuric acid was added to dissolve the precipiated alumina. The contents of the flask were transferred to a separatory funnel, and the aqueous phase extracted twice with 50-ml portions of ether. The combined ether solutions were dried over magnesium sulfate for 12 hours and distilled. The product, 2-methyl-1-butanethiol, was a slightly yellow liquid, b. p. 135° - 138°. This was redistilled and collected at 116° - 119°, n_D^{20} 1.4865, the yield was 2.5 g (0.024 mole, 25%).

Preparation of 2-Methyl-1-butanethiol from 2-Methyl-1-butanol

2-Methyl-1-butyl bromide was prepared as described by Milburn and Truter.[1] Phosphorus tribromide (22 g, 0.08 mole, Eastman Kodak No. 1354) was added slowly to an efficiently stirred solution of 2-methyl-1-butanol (18 g, 0.2 mole, Eastman Kodak No. 1956) in pyridine (5.5 g, 0.07 mole, Brothers Chemical Company, Karl Fisher grade) at 0°. The crude product was distilled under 100 mm pressure, dissolved in light petroleum ether (b. p. 30° - 60°), washed successively with 5% aqueous sodium hydroxide, 10% sulfuric acid, concentrated sulfuric acid, and water. The solution was dried and distilled to give 26.5 g (0.18 mole, 86% yield) of 2-methyl-1-butyl bromide, b. p. 119° - 121°, n_D^{20} 1.4450.[2]

The 2-methyl-1-butyl bromide was converted into 2-methyl-1-butanethiol with thiourea as outlined by Urquhart, Gates and Connor.[3] A mixture of 10 g (0.07 mole) of the previously prepared 2-methyl-1- butyl bromide, 5.3 g (0.07 mole) of thiourea

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[1] A. H. Milburn and E. V. Truter, J. Chem. Soc., 3344 (1954).

[2] Physical constants agree with those reported by Milburn and Truter.

[3] E. C. Horning, "Organic Syntheses" (John Wiley and Sons, Inc., New York, 1955), first edition, Collective Volume III, p. 363.

(Eastman Kodak No. P-497), and 35 ml of 95% ethanol was refluxed on a steam bath for 12 hours. A solution of 4.4 g (0.11 mole) of sodium hydroxide in 40 ml of water was added, and the mixture refluxed for 5 hours. The solution then was acidified with dilute sulfuric acid (7 ml of concentrated acid to 50 ml of water). The layers were separated and mercaptan layer distilled from a modified Claisen flask. The fore-run contained water and mercaptan. The yield of 2-methyl-1-butanethiol, n_D^{20} 1.4435, b. p. 116° - 118°,[1] was 4.6 g (0.043 mole 64% yield).

Unfortunately, the first attempt to prepare the 2,4-dinitrophenyl thioether derivative from the mercaptan obtained from the chlorosulfonylation gave the dinitrophenyl derivative of methanol, which was used as a solvent as recommended by Cheronis.[2] There was not time to prepare more of the mercaptan, however, it is clear that tert-amyl mercaptan was not formed (n_D^{20} 1.4379, b. p. 78°).[3] If Helberger were right, the tertiary mercaptan would result.

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[1] In agreement with that reported by A. Brjuchonenko, J. prakt. Chem., (2) 59, 45-52, 596 (1899).

[2] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis " (Thomas Y. Crowell Co., New York, 1947), first edition, p. 321.

[3] H. R. Rheinboldt, M. Dewald, and O. Diepenbruck, J. prakt. Chem., (2) 130, 133-46 (1931).

Preparation of 4-Chloro-2-methyl-1-pentanesulfonyl Chloride

A mixture of 357 g (3.5 moles) of 4-methyl-2-pentanol (Eastman Kodak No. P-3607) and 450 ml of C. P. concentrated hydrochloric acid (s. g. 1.18 - 1.19) was placed in a one-liter, round bottom flask fitted with a reflux condenser and a glass stirring rod connected to a mechanical stirrer. The homogenous solution then was heated with stirring on a steam bath for six hours. At the end of this reaction period two layers had formed. The upper layer was decanted into a separatory funnel, washed with several portions, each of about 75 ml of water and dried with calcium chloride overnight. Distillation of the mixture through a long column packed with glass helices gave 110 g (0.81 mole, 25% conversion) of 4-chloro-2-methylpentane, b. p. 111° - 113°, n_D^{20} 1.4125 (literature,[1] b. p. 111° - 112°/723 mm, n_D^{20} 1.4113).

In analogous manner to that described for isopentyl chloride, 180.8 g (1.5 moles) of 4-methyl-2-pentyl chloride was chlorosulfonylated. At the end of 27 hours reaction and after being washed and dried, the product was distilled under 15 mm through a Claisen flask. The distillate boiling at 154° - 165° was twice redistilled

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[1] F. C. Whitmore and F. Johnson, J. Am. Chem. Soc., 60, 2265 (1938).

through a short Vigreux column (11.5 cm x 4 cm). The physical properties were, b. p. 119° - 121°/4 mm, n_D^{20} 1.5040, d_4^{20} 1.401, M_D 46.3 (theory 49.2), 40.5 g (0.19 mole, 12.5% conversion based on alkyl chloride used) of the sulfonyl chloride being obtained. According to flowmeter readings, an excess of chlorine (3.3 moles) was used. However, the absence of excess decomposition during distillation and the small amount of residue indicate this figure is in error, otherwise there would have been a large amount of residue of polysulfonyl chlorides.

Anal.[1] Calc'd for $C_6H_{12}SO_2Cl_2$: C, 32.89%; H, 5.53%
Found: C, 28.49%; H, 4.38%.

Since the molar refraction and analysis do not agree with the theoretical values, a gas chromatogram was run on some of this material.[2] A Perkin-Elmer Model 154 vapor Fractometer was used with a packing of Apiezon L on fluebrick (packing QX) at 190°. Helium was used as elutant gas for the 0.005-ml sample under a column pressure of 10 p. s. i. The flowmeter was set at a reading of 5.2, the detector voltage at 8.0. The resulting curve showed the presence of but one compound. Desirable as correct ultimate analysis might be, the analytic discrepancy does not invalidate the structure proof.

Infrared data show characteristic sulfonyl chloride absorption bands at 1175 (8.50 μ) and 1385 (7.22 μ) cm^{-1}.[3]

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[1] Clark Microanalytical Laboratory, Urbana, Ill., reference number 42055, August 8, 1960.

[2] I am indebted to O. L. Gumprecht, Research Laboratory, Reichhold Chemicals, Inc., Tuscaloosa, Alabama, for the gas chromatogram.

[3] Bellamy, op. cit.

Preparation of 4-Hydroxy-2-methyl-1-pentanesulfonic acid sultone

4-Hydroxy-2-methyl-1-pentanesulfonic acid sultone was prepared from the corresponding sulfonyl chloride in a manner similar to that described earlier for the 4-hydroxy-2-methyl-1-butanesulfonic acid sultone. Thus 10 g of 4-chloro-2-methyl-1-butanesulfonyl chloride was heated for 30 hours with 25 ml of water under reflux. After distilling off the water, the brown syrupy 4-chloro-2-methyl-1-pentane sulfonic acid then was heated under 15 mm at 230°. After the evolution of hydrogen chloride the crude sultone distilled over as a colored liquid at 140° - 147°/5 mm. After being washed and dried the compound was solidified in liquid air. The produce was recrystallized from a mixture of carbon tetrachloride and isooctane. Unfortunately, there was not time to obtain the sultone as a sharp-melting solid. However, it is believed that the compound will melt higher than 45°, as reported by Helberger,[1] but in the range 46° - 47° as quoted by Heller.[2]

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[1] Helberger, Manecke, and Fischer, *loc. cit.*

[2] Heller, *op. cit.*

Conversion of 4-Chloro-2-methyl-1-pentanesulfonyl Chloride to 2-Methyl-1-pentanethiol

In a manner analogous to that described for 4-chloro-2-methy-1-butanesulfonyl chloride, 22 g (0.1 mole) of 4-chloro-2-methyl-1-pentanesulfonyl chloride in 143 ml (100 g) of dry ether was added to a 0.5 molar stock solution (300 ml, 0.5 mole) of lithium aluminum hydride and reduced to the corresponding mercptan. After work-up, the product, 2-methyl-1-pentanethial, was distilled through a Claisen flask, b. p. 140° - 143°, n_D^{28} 1.4452, yield 3.2 g (0.02 mole, 22%).

Preparation of 2-Methyl-1-pentanethiol from 2-Methyl-1-pentanol

2-Methyl-1-pentanol (Matheson, Coleman and Bell, P-8066) was distilled through a long column packed with glass helices; only the distillate boiling at 148° was collected. In an anaogous manner to that described for 2-methyl-1-butyl bromide, phosphorus tribromide (22 g, 0.08 mole, Eastman Kodak No. 1354) was added slowly to an efficiently stirred solution of 2-methyl-1-pentanol (20 g, 0.2 mole) in pyridine (5.5 g, 0.07 mole, Brothers Chemical Company, Karl Fisher grade) at 0°. The crude product was distilled under 100 mm pressure and dissolved in light petroleum ether (b.p. 30° - 60°). The solution was washed, dried, and distilled to give 23 g (0.14 mole, 70% yield) of 2-methyl-1-pentyl bromide, b. p. 144° - 146°.

The bromide was converted into 2-methyl-1-pentanethiol as previously described. A mixture of 23 g (0.14 mole) of the previously prepared 2-methyl-1-pentyl bromide, 12.2 g (0.16 mole) of thiourea (Eastman Kodak No. P-497) and 80 ml of 95% ethanol was refluxed on a steam bath for 24 hours. A solution of 10.2 g (0.25 mole) of sodium hydroxide in 92 ml of water was added, and the mixture refluxed for 10 hours. After acidification with dilute sulfuric acid, the layers were separated and the mercaptan layer distilled from a modified Claisen flask. The yield of 2-methyl-1-pentanethiol, n_D^{20} 1.4500, b. p. 141° - 143°,[1] was 9 g (0.076 mole, 60% yield).

Again, it is clear that tert-hexyl mercaptan was not formed, if it had been the boiling point would have been much lower. Unfortunately, the 2,4-dinitrophenyl thioether derivative from the mercaptan obtained from chlorosulfonylation gave the dinitrophenyl derivative of methanol. There was not time to prepare more of the mercaptan.

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[1] Erlenmeyer and Wanklyn, Ann., 135, 150; Ref. cit., "Beilstein Organische Chemie," (Edwards Brothers, Inc., 1942) H, 1, 409.

SUMMARY

Several discrepancies in the literature concerning the synthesis of tertiary sulfonyl chlorides are discussed. Contrary to published reports, it was shown that this type of compound is not obtained by photochemical chlorosulfonylation.

The sulfonyl chlorides of isopentyl chloride and 4-chloro-2-methylpentane were prepared, isolated, and physical properties obtained for the first time. The physical properties as observed for 4-chloro-2-methyl-1-butanesulfonyl chloride are, b. p. 139° - 141°/15 mm, n_D^{20} 1.4906, d_4^{20} 1.3432, infrared bands at 1175 (8.50μ) and 1375 (7.30μ) cm^{-1}. The properties of 4-chloro-2-methyl-1-pentanesulfonyl chloride are, b. p. 119° - 121°/4 mm, n_D^{20} 1.5040, d_4^{20} 1.401, infrared bands at 1175 (8.50μ) and 1385 (7.22μ).cm^{-1}.

Each sulfonyl chloride was reduced with lithium aluminum hydride to the unsubstituted mercaptan. These were shown to be 2-methyl-1-butanethiol and 2-methyl-1-pentanethiol by unequivocal syntheses of these mercaptans.

One new compound was synthesized: 4-chloro-2-methyl-1-pentanesulfonyl chloride. Reported for the first time are the physical properties of 4-chloro-2-methyl-1-butanesulfonyl chloride and 4-chloro-2-methyl-1-pentanesulfonyl chloride.

APPENDIX

September 24, 1956

Dr. Friedrich Asinger and/or
Dr. Gerhard Geiseler
Hauptlaboratorium der Leuna-Werke
Leuna, Merseburg
East Germany

Dear Dr. Asinger and/or Geiseler,

Please forgive the double salutation; it is just that I am not certain that Dr. Asinger is at the Leuna-Werke again, that Ber., 89, 1100 is completion of some work in which Dr. Asinger has taken an earlier part. At any rate, I am glad to see resumption of the work and hope that Dr. Asinger is at Leuna again. If a reprint is available, I will be grateful for a copy of "Über die Abhängigkeit der Reaktionsfahigkeit funtioneller Gruppen in Paraffinkohlenwasserstoffen von ihrer Stellung in der Molekel, II. Mitteil. Der Einfluss der Kettenlange des Alkylrestes auf die Hydrolysegeschwindigkeit primarer und sekundarer Mono- und Disulfochloride."

Earlier I have written to Dr. Asinger asking further experimental details of Asinger and Ebeneder, Ber. 75, 344 (1942). If either of you will give me more explicit instructions, I will be grateful, Several times we have tried to duplicate the conversion reported in this publication of the alkali salt of tertiary isobutanesulfonic acid to the corresponding sulfonyl chloride with phosphorus pentachloride. The directions mention only stirring the two solids together, followed by "the usual working up". It is entirely possible that the conventional technique employed is different from those that we have tried. Except for this one preparation, we have rather completely studied steric effects and, naturally, we want to get the whole picture.

Thank you very much for any help you may give.

Sincerely,

Robert B. Scott, Jr.
Professor of Organic Chemistry
University of Alabama
University, Ala.
U. S. A.

Prof. Dr.-ing.habil.
FRIEDRICH ASINGER

LEUNA, den 2. 10. 1956
Erich-Dehnel-Strabe 22

Herrn
Prof. Dr. Robert B. Scott jr.
University of Alabama
School of Chemistry

Alabama / USA

Sehr geehrter Herr Professor Scott!

Ich danke Ihnen für Ihr Schriben vom 24. Sept. und sende Ihnen in der Beilage den gewünschten Sonderdruck und erlaube mir gleichzeitig, auch noch andere Arbeiten aus der letzten Zeit Ihnen zu ubermitteln.

Was die Überführung der ter.-Butansulfosäure in das betreffende Sulfochloride anbetrifft, die in einer Arbeit von mir und Ebeneder (B. 75, 344 1942) beschrieben ist, so sind schon bezüglich der Wiederholung in mehreren Laboratorien Schwierigkeiten aufgetreten, und auch uns war es nicht leicht möglich, das entsprechende tert.-Amylsulfochlorid auf diese Weise zu bereiten. Die Reaktion läbt sich nur dann zufriedenstellend durchführen, wenn man die Einwirkung des Phosphorpentachlorids auf das betreffende Sulfonat unter auberordentlich starker Kühlung und gutem Rühren vornimmt.

Ich verbleibe mit den besten Grüben.

ihr sehr ergebener

/s/ F. Asinger

Anlagen

TRANSLATION

Prof. Dr. - Ing. habilitated
Friedrich Asinger

Leuna, den 2.10.1956
Erich-Dehnel-Strasse 22

Prof. Dr. Robert B. Scott jr.
University of Alabama
School of Chemistry
Alabama, USA

My dear Professor Scott!

I thank you for your letter of Sept. 24 and send you in addition the desired reprint, and allow me as well to send you also still other recent papers.

Concerning the conversion of tert-Butanesulfonic acid into the respective sulfonyl chloride, which is described in a paper by me and Ebeneder (Ber. 75, 344 (1942)), so difficulties have occurred in several laboratories even relative to the repetition (of our work), and also it was not easily possible for us to prepare the corresponding tert-Amysulfonyl chloride in this way. The reaction is satisfactorily carried out then only if the action of the phosphorus pentachloride on the respective sulfonate is carried out with extraordinarily strong cooling and good stirring.

I remain with best wishes your very obedient

F. Asinger (s)

E. I. DuPONT DE NEMOURS and COMPANY
WILMINGTON 98, DELAWARE

Organic Chemicals Department
Research Division
Experimental Station

November 14, 1956

Dr. Robert B. Scott, Jr.
University of Alabama
School of Chemistry
University, Alabama

Dear Bob:

Thanks very much for your letter on the preparation of _t_-butanesulfonyl chloride. As you will recall, I tried to repeat Asinger's preparation years ago and failed. I don't know just what he means by "extraordinarily strong cooling" but I remember I ran the reaction at about -20°C. without success. I hope you have better luck with the procedure than I did.

With best regards,

Sincerely,

/s/ Madison Hunt

/t/ Madison Hunt
Director

asm

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PROOF OF STRUCTURE OF SOME CONTROVERSIAL SULFONYL CHLORIDES

by

GEORGE BAKER McKEOWN

AN ABSTRACT

Submitted in partial fulfillment of the requirements for the degree
of Master of Science in Chemistry in the School of Chemistry
in the Graduate School of the University of Alabama

UNIVERSITY, ALABAMA

1960

PROOF OF STRUCTURE OF SOME CONTROVERSIAL SULFONYL CHLORIDES

An Abstract

Several discrepancies in the literature concerning the synthesis of tertiary sulfonyl chlorides are discussed. Contrary to published reports, it was shown that this type of compound is not obtained by photochemical chlorosulfonylation.

The sulfonyl chlorides of isopentyl chloride and 4-chloro-2-methylpentane were prepared. Each was reduced with lithium aluminum hydride to the unsubstituted mercaptan. These were shown to be 2-methyl-1-butanethiol and 2-methyl-1-pentanethiol, respectively, by unequivocal syntheses of these mercaptans.

A new compound, 4-chloro-2-methyl-1-pentanesulfonyl chloride, was synthesized, and 4-chloro-2-methyl-1-butanesulfonyl chloride, which is not a new compound, was isolated and characterized for the first time.