[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE STANDARD OIL DEVELOPMENT COMPANY]

A NEW PETROLEUM BY-PRODUCT: OCTANE-SULTONE

BY E. L. BALDESCHWIELER AND H. A. CASSAR

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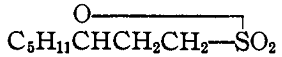
In the process for the manufacture of the higher secondary and tertiary alcohols such as *iso*propyl, secondary butyl, amyl and hexyl alcohols, etc., as used in the alcohol plant of the Bayway Refinery of the Standard Oil Company of New Jersey, the permanent gases from the stills are scrubbed first through a strong solution of sulfuric acid. The unsaturated compounds such as olefins are thus extracted by the acid. The latter is then diluted with water and hydrolysis takes place with the separation on the surface of a dark liquid of a very disagreeable odor and of high sulfur content. The latter is then drawn off and on cooling and standing deposits a black material. From this substance a new compound has been separated by extraction with hot benzol and precipitation with gasoline, whereupon a large crop of crystals was obtained which were found to consist of a single compound of the empirical formula $C_8H_{16}SO_3$ melting at 129.[1]



Structural Formula.—The structural formula $C_5H_{11}\overset{\text{O}}{\text{CH}}CH_2CH_2—SO_2$ was assigned to this compound from the data and deductions given below.

The empirical formula is $C_8H_{16}SO_3$, and molecular weight determinations show the compound to be monomolecular.

The compound does not form salts with dilute alkalies in the cold and reacts neutral to indicators; therefore it does not contain a free acid group.

The compound reacts acid on boiling with water; therefore it must contain an acid group bound up with an hydroxyl group, since the compound does not contain nitrogen.

The compound gives no bromine number and so does not contain an unprotected double bond; it cannot be brominated in a boiling solution of acetic acid and sodium acetate, and therefore can scarcely contain an aromatic nucleus.

The compound is not attacked by boiling acetyl chloride and hence can scarcely contain any free hydroxyl groups.

The compound on heating with dilute sulfuric acid under pressure and also on distillation over caustic potash liberates sulfur dioxide and yields a number of isomeric octanes and octenes boiling mainly around 110 to 116°; this splitting off of sulfur dioxide is characteristic of sulfonic acids.

On refluxing the compound with barium hydroxide a barium salt is obtained, the analysis of which agrees with the formula

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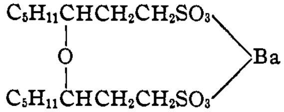
[1] The compound was isolated by E. L. Baldeschwieler, who first purified it and determined its empirical formula and physical constants; the chemical properties and structure were worked out by H. A. Cassar.



This formula represents the anhydride of the barium salt of an hydroxyoctanesulfonic acid. All attempts to prepare the hydrated compound failed; the silver salt was prepared by double decomposition from the barium salt and the potassium salt from the original compound by means of potassium hydroxide. These salts were found to be anhydrides, too, and were prepared to determine whether the double valency of the barium atom might have had any effect in promoting closure of the ring with elimination of the elements of water; this effect was not observed to take place.

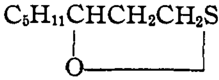
In a further search for the hydrated salt hydrolysis with mild alkalies was tried, but sodium carbonate yields the same salt, and barium carbonate yields a crystalline salt which is also anhydrous and a sirup, both of which derivatives were proved to be different from the salt by barium hydroxide.

The simplest member of the oxysulfonic acids is oxyethanesulfonic acid (isathionic acid), $HOCH_2CH_2SO_3H$, and when the barium salt of this acid is heated to 190 it loses the elements of water and changes into di-isathionic acid (di-ethyl ether β,β'-disulfonic acid).[2] It is not surprising, therefore, that when dealing with a higher member of this series containing eight carbon atoms the anhydrides should be the compound obtained, as the stability of organic compounds diminishes with increase in the length of the carbon chain, and anhydrides are generally more stable than hydrates.

When the barium salt by barium hydroxide or the sirup by barium carbonate are treated with dilute mineral acids and refluxed, the original compound separates out.

This hydrolysis by means of dilute alkalies and reformation by means of acids is characteristic of carboxylic and sulfonic acid lactones; the great solubility of the alkaline salts incidentally excludes carboxylic acids altogether.

All that remains now is to determine whether the amyl grouping in the compound is a straight or a branched chain and to characterize it. Unfortunately this point is still obscure. The main difficulty is the lack of intermediate compounds such as amyl and hexyl halides and olefins of known constitution and well-defined methods for identifying them in small quantities, which makes the remaining part of the problem almost hopeless of solution at the present time.

Since we are dealing with a sulfonic acid lactone with an octane group in it, and since all sulfonic acid lactones so far prepared in the aromatic series are γ-lactones, we must have a compound of the structure  $C_5H_{11}\underset{O}{CH}CH_2CH_2SO_2$. The structure  $C_5H_{11}\underset{SO_2}{CH}CH_2CH_2O$ is highly im-

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[2] Carl, *Ber.*, **14**, 65 (1881).

probable since primary alcohols are known not to form sulfonic lactones (see below) and also all alcohols made from olefins and sulfuric acid are secondary or tertiary. This compound we propose to call octane-sultone to fall in line with the present accepted nomenclature in the aromatic series.

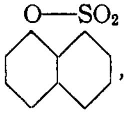
Naphthsultone,  , discovered by C. Mensching, examined by G. Schultz[3] and further investigated by H. Erdmann,[4] who invented the name sultone for this class of compound, contains three carbon atoms in the lactone group and is, therefore, a γ-sulfonic lactone. Ortho-phenol sulfonic acid, which could only give a β-sulfonic lactone, does not form a ring compound at all, but *o*-benzyl alcohol sulfonic acid forms a γ-sulfonic lactone called benzyl-sultone by the discoverers, W. Marckwald and H. H. Frahne.[5] All this leads one to expect the present sultone to be gamma; $CH_2OHCH_2CH_2SO_3H$ was also prepared by the latter co-workers and no lactone could be prepared from it, probably because the hydroxyl group is a primary alcohol.

TABLE I

SOLUBILITIES

	Octane-sultone	Benzyl-sultone	Naphthsultone
Cold water	Slight	Slight	?
Hot water	Medium	Medium	?
Cold alcohol	Slight	Slight	Slight
Hot alcohol	Very	Very	?
Chloroform, hot and cold	Very	Very	Very
Hot benzol	Very	Very	Very
Ligroin	Very slight	Very slight	?

Both octane-sultone and naphthsultone give flat transparent glassy crystals on slowly evaporating their benzol solutions, and all three can be sublimed; octane-sultone and benzyl-sultone are volatile in steam and naphthsultone distils unchanged.

All three sultones are dissolved by hot but not cold strong alkali, and the free acids of naphthsultone and benzyl-sultone are stable and are only changed back into the sultones by such drastic treatment as sublimation or phosphorus pentachloride, while octane-sultone changes from the free acid into the sultone by standing in warm dilute acid solutions overnight. Naphthsultone is not dissolved by alkali carbonates while octane-sultone is. As can be seen from the above comparison, the general properties of the three sultones are very similar.

Halogenation.—Octane-sultone cannot be brominated, but its alkaline salts, of which there are three varieties, absorb bromine very rapidly in

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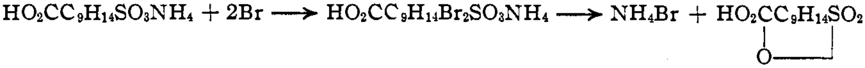
[3] Schultz, *Ber.*, **20,** 3162 (1887).

[4] Erdmann, *Ann.*, **247,** 344 (1888).

[5] Marckwald and Frahne, *Ber.*, **31,** 1898 (1898).

alkaline solution with reformation of the sultone ring. This is scarcely odd, since Géza Braun, for instance, found that the lactone of hydroxyisocrotonic acid had maximum ability to absorb bromine only immediately after saponification.[6] Also, when ammonium hydrogen sulfocampholenecarboxylate is treated with bromine in aqueous solution, a white precipitate of the brominated sultone is thrown down.[7]



$$HO_2CC_9H_{14}SO_3NH_4 + 2Br \longrightarrow HO_2CC_9H_{14}Br_2SO_3NH_4 \longrightarrow NH_4Br + HO_2CC_9H_{14}SO_2 \text{—}O$$

Type A salt, obtained by hydrolysis of the sultone with barium or calcium hydroxide, with sodium or potassium hydroxide and with sodium or potassium carbonate, absorbs two atoms of halogen in aqueous solution, yielding a monohalogen derivative with immediate reformation of the sultone ring. The position of the halogen atom is unknown but it is probably adjacent to the sulfonic group. On refluxing these halogenated octanesultones with strong alkali, they hydrolyze to easily crystallizable salts of oxyhalogenoctanesulfonic acids; the halogen atom is not hydrolyzed off, even on fusion with caustic soda. All attempts to reduce the halogen atom failed; a zinc–copper couple is sufficiently alkaline to yield the zinc salt of the oxyhalogenoctanesulfonic acid. The free acid was prepared from the barium salt through the lead salt followed by hydrogen sulfide and was found to be extremely soluble in water and not to show any tendency to reform the sultone. It is probable that the halogen atom is next to the sulfonic group, the sulfonic group hindering the hydrolysis and reduction of the halogen group, and the halogen group hindering the ring-closing tendency of the sulfonic group.

Type B salt, obtained by hydrolyzing the sultone with barium carbonate, is a sirup, and absorbs halogens like those of Type A, yielding monohalogen derivatives with immediate reformation of the sultone ring. These halogenated sultones of Type B are isomeric with those of Type A, but either strong or mild alkali splits off the halogen atom as halogen acid and at the same time hydrolyzes the sultone ring to give a salt that cannot be crystallized. On treating this sirup with warm dilute mineral acids the unsaturated sultone is obtained that crystallizes from dilute alcohol in beautiful white needles.

Here too the double bond and hence the original halogen atom must be in close juxtaposition with the sulfonic group, probably in the β-position with respect to it as the unsaturated sultone, which does not absorb bromine in the ring form, absorbs one atom of halogen by displacement in the form of its alkaline salts to give an unsaturated halogenated octane-sultone; here too the sultone ring is reformed at the instant of halogenation.

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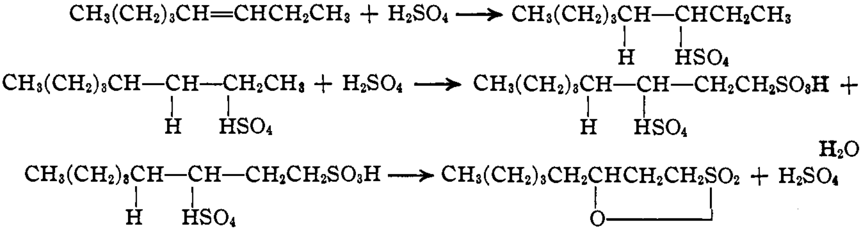
[6] Braun, This Journal, **51**, 241 (1929).

[7] Harvey and Lapworth, *J. Chem. Soc.*, **83**, 1102 (1903).

Enough is already known about unsaturated sulfonic acids in the aliphatic series to make this reaction seem plausible; for ethylene sulfonic acid absorbs bromine by substitution and not by addition.[8]

Type C salt, obtained by hydrolyzing the sultone with excess barium or calcium carbonate, is easily crystallized; it is completely isomeric with salts of Type A, being also the salt of an anhydride; treating this salt with warm dilute mineral acids does not give back the original sultone as with Types A and B but the sulfonic group is split off and an olefin boiling at 113 to 115° is obtained. Also, on halogenation the sulfonic group is split off and a mixture of octane mono and di-halides is the result. On treating salts of Type C with free iodine in warm aqueous solution alkyl iodides are obtained which decompose readily on steam distillation to olefins, which indicates that these alkyl halides are secondary or tertiary derivatives, since primary iodides as a rule can be steam distilled.

Octane-sultone, unlike carboxylate lactones, is not attacked by phosphorus pentachloride or acetyl chloride; the alkaline salts Types A and B are decomposed by the former and changed back by the latter into the original sultone.

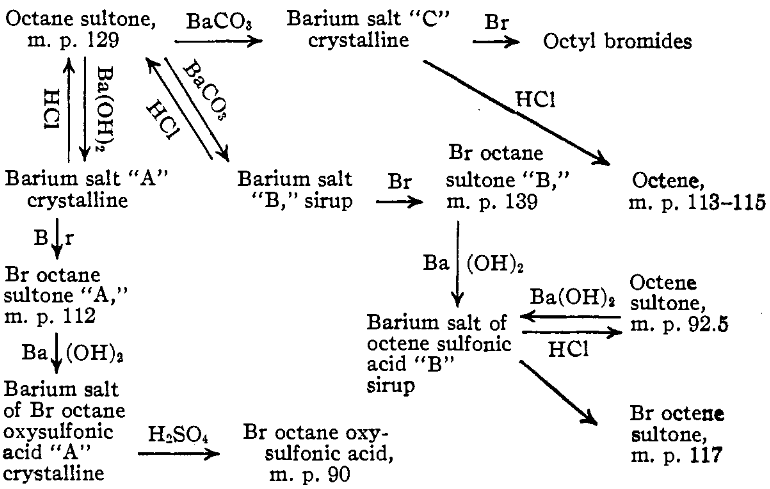


$$CH_3(CH_2)_3CH{=}CHCH_2CH_3 + H_2SO_4 \longrightarrow CH_3(CH_2)_3\underset{H}{\underset{|}{CH}}-\underset{HSO_4}{\underset{|}{C}}HCH_2CH_3$$

$$CH_3(CH_2)_3\underset{H}{\underset{|}{CH}}-\underset{HSO_4}{\underset{|}{CH}}-CH_2CH_3 + H_2SO_4 \longrightarrow CH_3(CH_2)_3\underset{H}{\underset{|}{CH}}-\underset{HSO_4}{\underset{|}{CH}}-CH_2CH_2SO_3H + H_2O$$

$$CH_3(CH_2)_3\underset{H}{\underset{|}{CH}}-\underset{HSO_4}{\underset{|}{CH}}-CH_2CH_2SO_3H \longrightarrow CH_3(CH_2)_3CH_2\underbrace{CHCH_2CH_2SO_2}_{O} + H_2SO_4$$

REACTIONS OF OCTANE-SULTONE



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[8] E. P. Kohler, *Am. Chem. J.*, **20**, 680 (1898).

The formation of this octane-sultone in the alcohol plant is still rather obscure; ordinary ethyl alcohol is known to react with fuming sulfuric acid by the well-known carbyl sulfate reaction to yield an hydroxyethylsulfonic acid and a similar reaction might occur here. Another explanation is given in the preceding series of reactions.

Experimental

Extraction and Purification of the Octane-sultone.—The crude material is grayish black and so finely divided as to appear amorphous. It was pulverized in a mortar with repeated additions of cold gasoline until all odor of the original mother liquor was removed as well as any adhering oil, that is, until the last gasoline wash became colorless. The residue was then extracted with boiling 90% benzol and filtered. A fine crop of crystals was produced by adding three volumes of gasoline to the benzol solution. The precipitation under these conditions is practically complete after standing overnight. The excess solvent was drained from the crystals, the latter were redissolved in benzol and again precipitated with three times the volume of gasoline. The gasoline used was normal benzine, a specially treated and steam distilled product which was free from heavy oils and unsaturated compounds. The process was repeated, the resulting crystals were dried for two days at 85°, pulverized and dried again overnight at 85°.

Anal. Calcd. for $C_8H_{16}SO_3$: C, 49.97; H, 8.33; S, 16.75; O, 24.95. Found: C, 49.70; H, 8.64; S, 16.73; O (by difference), 24.93; N, none; ash, none.

The molecular weight was determined by the freezing-point method using benzol as solvent and was found to be 188 as compared with the theoretical molecular weight, 192.

The compound is very stable; it has a very faint camphor-like odor, especially when heated. It melts sharply at 129° and sublimes without decomposition when melted in small quantities. When melted in large quantities, partial decomposition takes place with evolution of sulfur dioxide and a black tarry mass is left behind. It distils very readily with steam and can also be purified by crystallization from hot water, from which it comes out in long prismatic needles belonging to the monoclinic system. It can also be purified by evaporation of the benzol solution.

TABLE II

SOLUBILITY IN VARIOUS SOLVENTS

Solvent	Temp., °C.	Wt. %	Solvent	Temp., °C.	Wt. %
Water	100	1.55	Methyl alcohol	20	13.15
Water	20	0.025	Abs. ethyl alc.	20	4.98
Ethyl ether	20	4.84	Ethyl alc. 95%	20	5.21
Benzene, 90%	20	25.88	*Iso*propyl alc.	20	4.37
Chloroform	20	55.57	Normal benzine (above)	20	0.22
Acetone	20	52.43			

Specific gravity at 20°, 1.2973.

The yield from the original material as obtained from the refinery was as follows

Adhering oils	62.35%	soluble in benzol
$C_8H_{16}SO_3$	19.45%	
Residue	18.20%	insoluble in benzol
Total	100.00%	

The above insoluble residue, which was of a light gray color, was pulverized, dried at 60° and found to have the following composition

Analysis of residue insoluble in benzol

Ferrous sulfate	82.08%	
Sodium sulfate	1.40%	
Free sulfuric acid	0.26%	
Water of crystallization	13.16%	(by difference)
Silica	0.35%	
Basic ferrous sulfate	2.75%	(water insoluble)
Total	100.00%	

It is thought possible that the presence of such a large quantity of ferrous sulfate might help the formation of the sultone by maintaining reducing conditions in the solution.

Barium Salt Type "A" of Octane-sultone.—Fifty grams of octane-sultone is refluxed for four hours with 30 g. of barium hydroxide in 500 cc. of water in a 2-liter flask to avoid foaming over; the sultone goes completely into solution, the hot liquid is filtered to remove traces of insoluble matter, diluted with twice its volume of water to facilitate precipitation of the barium carbonate and saturated with carbon dioxide. The barium carbonate is filtered off and the liquid is carefully evaporated to dryness on the water-bath. It is purified for analysis by dissolving it in a mixture of absolute alcohol and ether, filtering and blowing air over the solution until crystals appear, when it is left in the ice box for an hour to finish the crystallization. The third or fourth recrystallization gives fine white needles. The salt can be crystallized from water but on drying it decomposes partially and the barium content is high. The silver salt is prepared by double decomposition of the barium salt with silver sulfate suspended in water, and is purified by crystallization from acetone. The potassium salt is prepared from octane-sultone and potassium hydroxide and is purified by dissolving in a mixture of absolute alcohol and benzol, adding gasoline and evaporating by blowing a current of air over the solution.

Anal. Calcd. for $C_{16}H_{32}O_7S_2Ba$: Ba, 25.50. Found: Ba, 25.58, 25.61, 25.57, 25.50. Calcd. for $C_{16}H_{32}O_7S_2Ag_2$: Ag, 34.97. Found: Ag, 35.22. Calcd. for $C_{16}H_{32}O_7S_2K_2$: K, 16.33. Found: K, 16.46.

Octane-sultone from Barium Salt Type "A."—Twenty grams of octane-sultone is refluxed for four hours with 10 g. of barium hydroxide and 100 cc. of water, the filtered solution is treated with enough sulfuric acid in the cold to precipitate all of the barium, then with enough concentrated sulfuric acid to make up a 5% solution and refluxed for an hour. The octane-sultone comes out as an oil that solidifies on cooling; yield of crude product, 10 g. The crude material is purified by recrystallization from alcohol and melted at 129°; a mixture of this substance and some of the original octane-sultone melted at 129°, too.

Bromo-octane-sultone Type "A."—Twenty-five grams of octane-sultone is refluxed with 200 cc. of a 15% solution of potassium hydroxide for twenty hours, or until all of the sultone is dissolved. To the cooled solution bromine is carefully added until the contents turn red, excess bromine is removed by acidifying and adding sodium sulfite, and the whole is cooled in ice until the pasty precipitate has turned brittle so that it can be collected on a Büchner funnel; yield of crude material, 34 g. against 35.3 g. theoretical. The compound is purified by crystallization from alcohol, from which solvent it comes out in fine white needles; m. p. 112°.

Anal. Calcd. for $C_8H_{15}BrSO_3$: C, 35.50; H, 5.57; S, 11.81; Br, 29.44. Found: C, 35.32; H, 5.67; S, 12.40; Br, 29.10.

The chlorine derivative was made in the same way, chlorine gas being bubbled into the solution until a test sample did not decolorize bromine water; m. p. 122.5°.

Anal. Calcd. for $C_8H_{15}ClSO_3$: C, 42.46; H, 6.66; S, 14.12; Cl, 15.62. Found: C, 42.86; H, 6.86; S, 13.99; Cl, 15.68.

From 0.1 to 0.3 g. of the purified barium salt of the octane-sultone Type "A" was dissolved in water and titrated with $N/10$ bromine in glacial acetic acid. The end-point is so sharp that a back-titration is not required, the first appearance of a faint yellow color persisting for a few minutes being taken as the end-point. The atoms of bromine required per molecule of $C_{16}H_{32}S_2O_7Ba$ were in one case 3.98 and in another case 3.96. This indicates that the reaction proceeds thus

$$C_{16}H_{32}S_2O_7Ba + 2\ Br_2 \longrightarrow 2C_8H_{15}BrSO_3 + BaBr_2 + H_2O$$

The same bromine derivative was made from solutions prepared by hydrolyzing octane-sultone with barium hydroxide, with sodium hydroxide or with sodium or potassium carbonate in 20% concentration.

Hydrolysis of the Bromo-octane-sultone Type "A."—Fifty grams of bromo-octane-sultone Type "A" was refluxed with one liter of water, to which was added 1.5 moles of barium hydroxide, for two hours or until the bromine derivative went into solution; the liquid was filtered hot and allowed to cool, when a crop of the barium salt crystallized out and was purified by crystallization from alcohol. The potassium salt was prepared in the same way. They are both anhydrous.

Anal. Calcd. for $C_{10}H_{30}Br_2S_2O_7Ba$: Ba, 19.73. Found: Ba, 19.77, 19.85, 19.72. Calcd. for $C_{16}H_{30}Br_2S_2O_7K_2$: K, 12.27. Found: K, 11.64.

Preparation of Free Bromo-octane-oxysulfonic Acid.—The barium salt of the sulfonic acid was changed into the free acid by dissolving it in water, in which it is quite soluble, adding a slight excess of sulfuric acid to precipitate all the barium, boiling the filtrate with lead carbonate to remove excess sulfuric acid, filtering, precipitating the lead with hydrogen sulfide, refiltering and carefully concentrating on the water-bath to a sirup, which crystallizes in a few days. This solid is then dried by pressing onto porous plates and is purified by crystallizing several times from benzol; m. p. 90°. The presence of slight traces of mineral acids in the solution gives the compound a purple color.

Barium Salt Type "B" of Octane-sultone.—Twenty-five grams of octane sultone was refluxed for twelve to sixteen hours with 14 g. of barium carbonate and 50 cc. of water, the hot liquid is filtered to remove traces of insoluble matter, and cooled. Should any of the barium salt crystallize out it is removed, as the crystallizable salt is Type "C;" the filtrate can be concentrated down to a sirup but will not crystallize out.

Bromo-octane-sultone Type "B."—The sirupy barium salt Type "B" is diluted with water and to the cooled solution bromine is added until the upper layer turns red, excess bromine is removed by acidifying and adding sodium sulfite and the whole is cooled in ice until the pasty precipitate has turned brittle so that it can be collected on a Büchner funnel. A certain amount of a brominated oil will always be formed and run through the Büchner funnel into the receiver; this comes from the barium salt Type "C" which is always present to a certain extent. The precipitate is purified by crystallization from alcohol, from which solvent it comes out in fine white needles; m. p. 139°. The chlorine derivative is made in the same way; m. p. 118.5°.

Anal. Calcd. for $C_8H_{15}BrSO_3$: C, 35.50; H, 5.57; S, 11.81; Br, 29.44. Found: C, 35.65; H, 5.80; S, 12.30; Br, 29.49; 29.32, 30.00.

Anal. Calcd. for $C_8H_{15}ClSO_3$: C, 42.46; H, 6.66. Found: C, 42.79; H, 6.90.

Hydrolysis of Chloro-octane-sultone Type "B" and Subsequent Closing of Sultone Ring to Form Octene-sultone.—Ten grams of octane chloro-sultone Type "B" is refluxed with 15 g. of barium hydroxide in 80 cc. of water for an hour, the solution is cooled, a slight excess of sulfuric acid is added and the barium sulfate filtered off. Ten cc. of concentrated sulfuric acid is then added to the filtrate, which should amount to about 200 cc., and the acid solution is refluxed for an hour to close the sultone ring. The sultone comes out as an oil which solidifies on cooling; it is collected on a Büchner funnel and dried at 60°; yield, 7.3 g. of crude substance or 86% of the theoretical. The crude is purified by repeated crystallization from dilute alcohol, from which it comes out in beautiful white needles over an inch long; m. p. 92.5°.

Anal. Calcd. for $C_8H_{14}SO_3$: C, 50.59; H, 7.40; S, 16.79. Found: C, 50.67; H, 7.59; S, 17.26.

The barium salt of this unsaturated sultone is a sirup; hydrolysis of the chlorosultone lactone Type "B" in acid solution causes decomposition.

Preparation of Bromo-octene-sultone.—About ten to twenty grams of the sodium salt of octene sultone in aqueous alkaline solution is treated with bromine until a permanent yellow color is obtained. The precipitate is crystallized from alcohol; m. p. 117°.

Anal. Calcd. for $C_8H_{13}BrSO_3$: C, 35.77; H, 4.87; S, 11.97; Br, 29.66. Found: C, 35.93; H, 5.13; S, 12.55; Br, 29.96.

Calcium Salt Type "C" of Octane-sultone.—Twenty-five grams of octane-sultone is refluxed with nine grams of calcium carbonate and 400 cc. of water overnight, the solution is filtered hot and concentrated. The calcium salt comes out in white pearly plates; yield, first crop, 9.8 g.; second crop, 9 g.; third crop, 7.5 g.

The barium salt was made in the same manner, using a larger excess of barium carbonate; the yield is not as good.

Anal. Calcd. for $C_{16}H_{32}O_7S_2Ba$: Ba, 25.50. Found: Ba, 25.21, 25.35.

Octyl Bromides.—On treating the above salts in alkaline solution with bromine a heavy oil is deposited that on distillation under vacuum gives a lighter fraction lighter than water and a heavier fraction heavier than water. Purification was not successful.

Octene.—Two hundred and fifty grams of the calcium salt of octane-sultone Type "C" was dissolved in 1000 cc. of water, a slight excess of sulfuric acid added to precipitate all the calcium and the mixture was steam distilled. An octene came over and was carefully fractionated twice; yield of crude olefin, 130 g. (61%). 96% of this olefin distils between 113 and 115°, the remainder between 110 and 113°. Repeated distillation does not effect a further separation. The olefin does not give a solid nitrosochloride.

Anal. Bromine absorbed: 171, 169 g. per 112 g. of olefin, as against 160 g. required for C_8H_{16}.

Acknowledgment.—The writers wish to express their appreciation and thanks to M. G. Gardella for his carbon and hydrogen determinations and to C. C. Callis for the molecular weight determination.

Summary

1. A compound of empirical formula $C_8H_{16}SO_3$ has been obtained from one of the by-products of the manufacture of alcohols at the Bayway Re-

finery of the Standard Oil Co. (N. J.) and separated as crystals of a high degree of purity.

2. The compound is undoubtedly an octane-sultone, since its behavior is strictly analogous to that of sultones in the aromatic and camphene series.
3. On refluxing with alkalies various alkaline salts are obtained whose different chemical properties are explained by a shifting of the double bond generated from the hydroxyl group.
4. Attempts are now being made to synthesize sultones in the aliphatic series.
5. The compound is interesting to the petroleum technologist as it is volatile in steam; hence aliphatic sultones may be partly responsible for the sulfur content of refined gasolines.

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[Contribution from the Department of Chemistry of the University of Pittsburgh]

REACTIONS OF VINYL CHLORIDE AND BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

By James M. Davidson with Alexander Lowy

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The purpose of this investigation has been to study the reactions of vinyl chloride and benzene in the presence of aluminum chloride, under variable conditions, in order to determine the course of the reactions and to study the products formed. These reactions seemed important since vinyl chloride has recently been prepared in large quantities.

Böeseken and Bastet[1] found that vinyl chloride and benzene condensed in the presence of a catalyst made from aluminum and mercuric chloride, and produced chiefly unsymmetrical diphenylethane and a small quantity of 9,10-dimethyldihydro-anthracene. Vinyl bromide and benzene were found to react in the presence of aluminum chloride by Angelbis and Anschütz,[2] and Anschütz,[3] and yielded the identical products described by Böeseken and Bastet. Hanriot and Guilbert[4] obtained products believed to have been β-bromo-ethylbenzene and *p*-di-(β-bromo-ethyl)-benzene in the same reaction.

From the nature of the Friedel–Crafts reaction, styrene would be expected as an intermediate in the reaction under consideration. Schramm[5] obtained unsymmetrical diphenylethane from the reaction between styrene, benzene and aluminum chloride, but Böeseken and

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[1] J. Böeseken and M. C. Bastet, *Rec. trav. chim.*, **32**, 184 (1913).

[2] A. Angelbis and R. Anschütz, *Ber.*, **17**, 165, 167 (1884).

[3] R. Anschütz, *Ann.*, **235**, 159, 299 (1886)..

[4] Hanriot and Guilbert, *Compt. rend.*, **98**, 525 (1884).

[5] J. Schramm, *Ber.*, **26**, 1709 (1893).