

the stage at which the fruit was picked. Furthermore, it is evident that even in cases where color is of no consequence and pungency is of first consideration, fully matured fruit must be used to obtain the maximum value.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

DERIVATIVES OF ANTHRAQUINONE. ALIPHATIC THIO-ETHERS, DITHIO-ETHERS, AND THIO-ETHER SULFONIC ACIDS.

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Introduction.

The original object in taking up the study of anthraquinone sulfonic acids was to obtain derivatives which could be used for their ready separation and identification. This object was only partially attained but the reaction tried proved interesting and the products obtained appeared worthy of study, so the investigation was shifted from its original purpose and extended in other directions.

On account of the instability of the esters of sulfonic acids the methods used for the identification of carboxy acids² were not promising and our efforts were directed to the replacement of the sulfonic groups.

It was known that the sulfonic acid group of α -anthraquinone sulfonic acids can be replaced by methoxy³ or phenoxy⁴ groups, and that the resulting compounds $C_{14}H_7O_2.OCH_3$ and $C_{14}H_7O_2.OC_6H_5$ are crystalline and have definite, though rather high melting points. Hence it was thought that a compound of the type $C_{14}H_7O_2.SR$ would be of service. *N*-butyl mercaptan was used as being readily available, and it was thought probable that the compound $C_{14}H_7O_2.SC_4H_9$ would have a low melting point, since sulfur compounds usually melt lower than the corresponding oxygen compounds, and since butyl derivatives are apt to melt considerably lower than methyl, and much lower than phenyl. The desired reaction was found to take place readily, although not quantitatively, when the sulfonic acid group is in the α -position. The resulting compounds were found to have convenient melting points suitable for the identification of anthra-

¹ The work on the 1,5-compounds is from the Doctor's dissertation (1920) of Colin M. Mackall and that on the 1,8-compounds from that of George E. Miller (1920); the α -derivatives were prepared by the other author with some assistance from W. S. Hoffman of this Laboratory and A. T. Frascati in the Laboratory of E. I. du Pont de Nemours and Company.

² THIS JOURNAL, 39, 124, 304, 701, 1727 (1917); 41, 75 (1919); 42, 1043 (1920); and 43, 629 (1921).

³ Bayer and Co., Ger. pat. 156,762.

⁴ Bayer and Co., Ger. pat. 158,531.

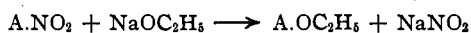
quinone- α -sulfonic acid, and anthraquinone-1,5- and -1,8-disulfonic acids.

Our study has been extended to the derivatives of other mercaptans.

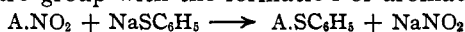
Historical.

Anthraquinone aliphatic thio-ether sulfonic acids and dithio-ethers may be prepared by the action of aliphatic mercaptans on anthraquinone sulfonic acids in alkaline solution.⁵ In this way Bayer and Company prepared anthraquinone-1-ethyl-thio-ether-5-sodium sulfonate and 1,5-diethyl-thio-ether.

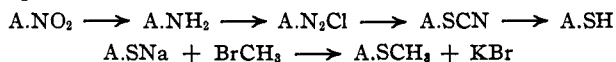
Gattermann⁶ has shown that the nitro group is replaceable by the alkoxy group when treated with sodium alcoholate, thus,



representing the anthraquinone residue by A. He attempted to carry out the analogous reaction with aliphatic mercaptans in order to obtain anthraquinone thio-ethers, but was hindered by the reduction of the nitro group to the amino group. On the other hand, he found that treatment with alkali aromatic mercaptides readily caused a quantitative replacement of the nitro group with the formation of aromatic thio-ethers.



Gattermann⁷ has also prepared anthraquinone aliphatic thio-ethers and thio-ether sulfonic acids indirectly by diazotizing amino-anthraquinones, or amino-anthraquinone sulfonic acids in conc. sulfuric acid. Subsequent treatment of the diazo compound with potassium thiocyanate yielded anthraquinone thiocyanate which on boiling with alcoholic potash gave the mercaptan, which with alkyl halide yielded the thio-ether or thio-ether sulfonic acid. In this way he prepared anthraquinone- α -methyl-thio-ether; anthraquinone- α -ethyl-thio-ether; anthraquinone-1-methyl-thio-ether-5-potassium sulfonate; and anthraquinone-1-methyl-thio-ether-8-potassium sulfonate, thus,



Outline of Present Investigation.

We have found that anthraquinone- α -sulfonic acid, and the 1,5- and 1,8-disulfonic acids, on heating with aliphatic mercaptans in alkaline solution, react readily to form anthraquinone thio-ethers, thio-ether sulfonic acids, and dithio-ethers, the sulfonic acid groups being replaced in turn.

This reaction takes place with great ease at 100° provided the concentrations are right. The formation of the product from the α -sulfonate

⁵ Bayer and Co., Ger. pat. 224,589.

⁶ Bayer and Co., Ger. pat. 75,054.

⁷ *Ann.*, 393, 113 (1912).

can be noticed within 2 to 10 minutes after adding the mercaptan. With the 1,5-disulfonate, the separation of the thio-ether monosulfonate begins within a few minutes on account of the very slight solubility of these compounds, while with the 1,8-disulfonate the reaction follows the same course except that the half-way product is much more difficult to obtain, on account of its greater solubility which favors the second stage of the reaction.

Gattermann found that α -C₁₄H₇O₂NO₂ reacts readily with potassium thiophenate, KSC₆H₅, to give α -A-SC₆H₅. We have endeavored to replace the sulfonic group by using phenyl mercaptan in the same way as the alkyl mercaptans but so far without result, though benzyl and *p*-nitrobenzyl mercaptans react readily under the regular conditions to give excellent yields of the corresponding thio-ethers.⁸

Several experiments have been made in the hope of finding the determining factor. The sodium salt of thioglycolic acid reacts readily but the sodium salt of thiolbenzoic acid does not. In this case the mixture was heated for about 40 hours but no sulfur dioxide was evolved on acidifying a test portion, showing that no sulfite had been formed. The thiolbenzoic acid could be recovered unchanged. This was tried with the 1,5-disulfonate for the same time but with similar negative results; however, there was some indication of a reaction with the 1,8-disulfonate though it had not gone far in 40 hours' heating.

In the hope of finding some compound with about the same acid strength as the aliphatic mercaptans, *m*-aminophenol was tried. This and the sulfonate were boiled with excess of caustic soda solution but there was no evidence of a reaction.

As the α -sulfonic acid group is somewhat more reactive than the β -group in naphthalene, sodium α -naphthalene sulfonate was boiled with butyl mercaptan and caustic soda solution, but no reaction took place.

The Compounds Obtained.

The anthraquinone thio-ethers and dithio-ethers are insoluble in water, slightly soluble in alcohol and soluble in benzene, the solubility in benzene increasing with the size of the alkyl group. When crystallized from benzene they form lustrous crystals varying in color from light yellow to red.

The corresponding sulfones are high melting, slightly yellow crystalline powders.

The anthraquinone-thio-ether sodium sulfonates are moderately soluble in water, the derivatives of the lower mercaptans being more soluble than those of the higher mercaptans and the 1,8 salts being considerably more soluble than the corresponding 1,5 salts. They crystallize from water in

⁸ Unpublished work of W. S. Hoffman.

orange or orange-red needles usually containing one molecule of water of hydration. Salts of other bases are highly colored, ranging from yellow through shades of orange to red and are mostly well crystallized.

In the 1,5 series of monobutyl-thio-ether sulfonates, the colors of the barium, strontium and calcium salts run in this order, the barium being deep red and the calcium salt orange, while in the corresponding 1,8 series the order of the colors is reversed.

Experimental.

Materials.—The anthraquinone- α -sodium sulfonate, and anthraquinone 1,5- and 1,8-disodium sulfonates were obtained through the courtesy of E. I. du Pont de Nemours and Company. The methyl mercaptan was generated as required by dropping dimethyl sulfate into warm sodium hydrosulfide, which was prepared by warming crystallized sodium sulfide, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, to about 90° and saturating with hydrogen sulfide. The ethyl mercaptan was prepared in a similar manner using sodium ethyl sulfate. The propyl, butyl and *iso*-amyl mercaptans were prepared by the catalytic method of Kramer and Reid.⁹

Analytical.

1. **Water of Hydration.**—One-g. samples were exposed to an atmosphere of 50% humidity¹⁰ for 48 hours, then heated to constant weight in a vacuum at 110° , 2 to 4 hours being generally sufficient to remove all the water. Analyses for sulfur and metals were made on the dry samples.

2. **Sulfur.**—Sulfur was determined by means of the Parr bomb,¹¹ using a 0.2 g. sample and 5 g. of sodium peroxide, with subsequent precipitation of barium sulfate.

3. **Sodium, Barium, Strontium, Calcium, Nickel and Cobalt.**—One-half g. samples were ignited in a platinum crucible until the carbon was burned off as completely as possible. The residue was then evaporated with conc. sulfuric acid, and re-ignited with ammonium carbonate to constant weight. The metal was weighed as the sulfate.

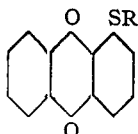
4. **Lead.**—Half-g. samples were ignited cautiously and the residue heated with nitric acid which was evaporated. The residue was evaporated with sulfuric acid and re-ignited with ammonium carbonate to constant weight, the metal being weighed as sulfate.

5. **Copper.**—The copper was precipitated in a faintly ammoniacal solution with hydrogen sulfide. The precipitate was filtered off, dried, ignited and weighed as cupric oxide.

⁹ Kramer and Reid, *THIS JOURNAL*, **43**, 880 (1921).

¹⁰ A dead air humidior containing 44% H_2SO_4 was used to obtain this humidity.

¹¹ Parr, *J. Ind. Eng. Chem.*, **11**, 230 (1919).

I. Anthraquinone α -Alkyl Thio-ethers.

One-fifth mole, or 62 g., of sodium anthraquinone α -sulfonate was heated with 1400 cc. of water containing 0.5 mole of caustic soda and a little more than 0.25 mole of the desired mercaptan. The solubility of sodium anthraquinone α -sulfonate is given by Dünschmann¹² as 5.1 g. per 100 cc. of boiling water but is diminished by the presence of the caustic soda, so that not quite all of the salt was in solution at the start. The methyl mercaptan was passed through in vapor form while the reaction mixture was heated to near its boiling point and mechanically stirred. The other mercaptans were added in liquid form, sometimes in portions, and the mixtures boiled under reflux. The acid character of the mercaptans is so weak that they readily distil out of the mixture even though it contains an excess of alkali. For this reason some excess of mercaptan was used, particularly of the more volatile ones. With propyl mercaptan 38 g. or 67% of the calculated amount of α -C₁₄H₇O₂.SC₃H₇, was obtained directly but the filtrate was boiled with 5 g. additional of mercaptan and 10 g. more of the product obtained, bringing the yield up to 85%.

The reaction takes place rapidly and considerable of the product can be observed within 2 to 10 minutes, but the mixtures were heated about 10 hours. The reaction mixtures were filtered hot and the sodium salts washed out with hot water. The anthraquinone-thio ethers were recrystallized from benzene or benzene and alcohol. The yields were good.

Details of several preparations are given in tabular form.

TABLE I.

PREPARATION OF Alkyl.	α -ALKYL Sodium sulfonate.	ANTHRAQUINONE			THIO-ETHERS, α -C ₁₄ H ₇ O ₂ .SR.	
		Water. Cc.	NaOH. G.	Mercaptan. G.	Yield. %.	%.
Ethyl	20	400	4	5	9	50
Ethyl	62	1500	20	20	47	88
Propyl	62	1500	20	19	48	85
Butyl	62	1400	20	23	55	93
<i>iso</i> -Butyl	62	1400	20	20	42	81
<i>iso</i> -Amyl	62	1400	20	26	53	86

TABLE II.

PROPERTIES AND ANALYSES¹³ OF ALKYL ANTHRAQUINONE THIO-ETHERS, α -C₁₄H₇O₂.SR.

Alkyl.	M. p. °C.	Sulfur.		Color and form.
		Calc. %.	Found. %.	
Methyl	221	12.66	12.31	reddish-orange needles
Ethyl	184	11.62	11.51	orange nd.
Propyl	151	11.40	11.36	orange nd.
Butyl	112.5	10.82	10.77	yellowish-red nd.
<i>iso</i> -Butyl	144	10.82	10.98	yellow
<i>iso</i> -Amyl	86	10.33	10.57	orange

The melting point goes down as the weight of the alkyl group increases.

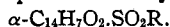
¹² Dünschmann, *Ber.*, 37, 331 (1904).

¹³ Melting points and analyses by W. S. Hoffman.

Gattermann gives the melting points of the methyl and ethyl derivatives as 208° and 183°.

Anthraquinone Thioglycolic Acid, $C_{14}H_7O_2.SCH_2COOH$.—A mixture of 31 g. of sodium α -anthraquinone sulfonate, 11.5 g. of thioglycolic acid, 10 g. of sodium hydroxide and 700 cc. of water was boiled for 11 hours. Crystals, 27 g., separated on cooling. These were filtered off and dissolved in hot water and the free acid precipitated by hydrochloric acid. They were recrystallized partly from nitrobenzene and partly from water and obtained as fine bright yellow needles, m. p. 243°, from which was prepared the sulfoxide, m. p. 239°; Gattermann gives m. p. 250° and 240°, respectively.

II. Anthraquinone α -Alkyl Sulfones.



The sulfones were prepared by oxidizing the thio-ethers by pouring over them enough fuming nitric acid to dissolve them, and pouring the solution into hot water. They may be purified by recrystallization from acetic acid. When prepared from pure thio-ethers they are obtained pure at the start and their melting points are not raised by recrystallization. All of them are slightly yellowish-white.

TABLE III.
ALKYL ANTHRAQUINONE SULFONES, $\alpha-C_{14}H_7O_2.SO_2R$.

Alkyl.	M. p. ° C.	Calc. %.	Sulfur.	Found. %.
Methyl	254	11.20		10.88
Ethyl	211.5	10.68		10.74
Propyl	204.5	10.20		10.30
Butyl	150	9.77		10.00
<i>iso</i> -Butyl	190	9.77		9.97
<i>iso</i> -Amyl	133	9.37		9.56

Gattermann gives the methyl and ethyl sulfones as melting at 251° and 210°.

III. Experiments with Sodium β -Anthraquinone Sulfonate.¹⁴

Only preliminary experiments have been made, as it was soon found that this subject must be left for further study. When the sulfonic acid group is in the β -position the replacement by the mercaptan residue takes place with much greater difficulty, if at all; such small quantities, only about 1.3%, of thio-ethers have been obtained, when the experiment is tried in the usual manner, that it is not certain whether the product is produced from the β -sulfonate or is derived from some impurity in it.

Two experiments were made on silver salt, using crude in one case and recrystallized in the other, boiling 1 kg. of the salt for 4 hours with 8 liters of water, 40 g. of caustic soda and 80 g. of butyl mercaptan. The reaction mixture was filtered hot and the residue extracted with chloroform which was then evaporated leaving a red mass that appeared to be a thio-ether. In each case the amount of this was 13 g. No substance of constant properties has so far been isolated from this, or from the supposed sulfone obtained by oxidizing it with fuming nitric acid. Analyses indicate the presence of a monothio-ether, and melting points as well as mixed melting points show conclusively that little, if any, of the α -thio-ether or its sulfone was present.

Dünschmann¹² separated some α -sulfonic acid, by recrystallization of the sodium salts, from the products obtained by sulfonating anthraquinone in the usual way without catalyst. Liebermann and Pleus¹⁵ showed that commercial "silver salt" contains some

¹⁴ Preparation of compounds by A. T. Frascati; melting points and analyses by W. S. Hoffman.

¹⁵ Liebermann and Pleus, *Ber.*, 37, 646 (1904).

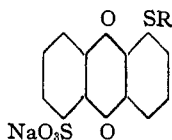
of the α -salt but in neither case was any information obtained as to the proportion of the α -salt except that its amount was small.

We sulfonated 208 g. of anthraquinone with oleum in the usual way and obtained 140 g. of silver salt (42.7%), and recovered 43.8% of the anthraquinone. The mercaptan reaction was tried as above with this silver salt and 1% of a thio-ether resembling that described above was obtained.

One-half of the mother liquor from which the silver salt separated was made alkaline and boiled with butyl mercaptan. The solution was filtered hot and the residue extracted with benzene which left 0.7 g. of a yellow thio-ether.

This melted at 89–92° and had the odor of butyl disulfide. It contained 11.64% of sulfur instead of 10.82% calculated for the butyl thio-ether. It was converted into the sulfone which melted at 150°; mixed with α -sulfone (m. p. 150°) it melted also at 150°. It contained 9.86% sulfur as compared with calculated 9.77%. Thus it is proved that the mercaptan derivative obtained from the sulfonation mother liquor is the α -thio-ether, confirming the presence of the α -acid as a product of the sulfonation of anthraquinone without catalyst. For the total mother liquor 1.4 g. would have been obtained representing 1 g. of anthraquinone or about 1% of that sulfonated. As the mercaptan reaction is not quantitative but usually yields about 80%, we may say that something over 1% of the sulfonic acid groups enter the α -position.

IV. Anthraquinone-1-alkyl-thio-ether-5-sulfonic Acid.



After several preliminary experiments with small quantities a mixture of 300 g. (or 0.61 mol.) of sodium anthraquinone-1,5-disulfonate ($1,5\text{-C}_{14}\text{H}_8\text{O}_2(\text{SO}_3\text{Na})_2 \cdot 5\text{H}_2\text{O}$), 36 g. (or 0.9 mol.) of caustic soda, 120 g. (or 1.0 mol.) of butyl mercaptan (75%) and 4500 cc. of water, was boiled under a reflux condenser for 11 hours, cooled and filtered. The residue was washed with three 800cc. portions of water and dried. From 800 cc. of wash water 1 g. of the barium salt was obtained by precipitation with barium chloride, showing that the sodium salt is soluble in about 1000 parts of cold water. The residue was extracted thrice with hot benzene which removed about 4 g. of the 1,5-anthraquinone-dibutyl-dithio-ether. Hence the yield is 95% of the calculated, while the dithio-ether formed amounts to only 1.6%.

As the monothio-ether-sulfonate, the first reaction product, is only slightly soluble even in hot water, its effective concentration is not enough to push the second reaction. Using ethyl mercaptan where the intermediate product is more soluble about 10% of the dithio-ether was obtained.

The anthraquinone-1-butyl-thio-ether sodium sulfonate obtained as above is a beautiful golden-yellow, with only a slight reddish tinge, closely resembling mosaic gold and we have called it the "gold salt" to correspond with the "silver salt" which is sodium β -anthraquinone sulfonate. Both of these salts lose their metallic sheen when recrystallized. The "gold salt" then appears as glittering orange-red needles.

This salt in a 2% bath dyes¹⁶ unmordanted wool a slightly orange-yellow. It is a bright attractive color and is fairly fast to light but not fast to washing and milling. The bath is exhausted by the wool. The tinctorial power is not sufficient for a valuable dye. With chromium as a mordant, wool is dyed a greenish-yellow. The corresponding ethyl derivative dyes unmordanted wool a pure yellow.

¹⁶ Experiments in the Dye Laboratory of E. I. du Pont de Nemours and Co.

If various metallic salts are added to the bath in which wool is being dyed with the sodium salt, various widely different colors may be obtained; thus a barium salt gives a red and a lead salt a chocolate-brown.

Although the butyl-thio-ether sodium sulfonate is only slightly soluble in hot water it is soluble enough so that other salts, particularly those of the heavy metals and of the aromatic amines, can be prepared from it by double decomposition. For this purpose the sodium salt is dissolved in boiling water and an equivalent amount of a neutral solution of some soluble salt of the desired base is added. The most of these salts are too insoluble to be recrystallized but soluble impurities can be removed by extraction with boiling water. Many such salts containing various alkyls have been thus prepared. The salts are lustrous and many of them highly colored.

The corresponding derivatives with other mercaptans were not so extensively studied. The details of these preparations of the sodium salts are given in tabular form. All of these salts contain one molecule of water.

TABLE IV.

PREPARATION OF ANTHRAQUINONE-1-ALKYL-THIO-ETHER-5-SODIUM SULFONATES.
1,5-RS.C₁₄H₆O₂.SO₃Na.H₂O.

Alkyl.	Sulfonate. G.	Water. Cc.	NaOH. G.	RSH.	Time. Hrs.	Yield. G.	%.
Methyl	50	400	13	gas	2	30	65
Ethyl	100	600	26	gas	1	38	42
Propyl	50	1000	10	12	1	23	50
Butyl	50	500	16	15	7	30	62
<i>iso</i> -Amyl	100	1000	32	34	15	55	55

TABLE V.

ANALYSES AND PROPERTIES OF SODIUM SALTS. 1,5-RS.C₁₄H₆O₂.SO₃Na.H₂O.

Alkyl.	Water.		Sodium.		Color and form.
	Calc. %.	Found. %.	Calc. %.	Found. %.	
Methyl	4.81	4.86	6.46	6.27	orange-red needles
Ethyl	4.64	4.93	6.21	6.04	dark orange-red needles
Propyl	4.48	4.42	5.98	5.92	rich orange-red needles
Butyl	4.33	4.41	5.77	5.77	orange-red needles
<i>iso</i> -Amyl	4.19	4.26	5.58	5.43	orange-red needles

Barium, Calcium and Strontium Salts.—These were made by dissolving the sodium salts in hot water and adding the calculated amounts of the chlorides of the other metals. The resulting salts are extremely insoluble and are purified by boiling out with water.

TABLE VI.

BARIUM SALTS. 1,5-(RS.C₁₄H₆O₂SO₃)₂Ba.

Alkyl.	Barium.		Color and form.
	Calc. %.	Found. %.	
Methyl	17.09	17.00	red needles
Ethyl	16.51	16.50	red crystal powder
Propyl	15.97	15.58	orange-red needles
Butyl	15.47	15.43	red crystals
<i>iso</i> -Amyl	14.99	14.56	red crystals

The strontium and calcium salts also were made of the butyl acid, the strontium salt being anhydrous, (Sr, calc. 10.45; found, 10.40). The calcium salt, unlike the others contains 4 molecules of water of crystallization, showing by analysis 8.12%

of water and 5.09% of calcium compared to 8.35 and 5.07% respectively, by formula. The barium salt is a deep red and the calcium salt an orange-red, while the strontium salt is intermediate.

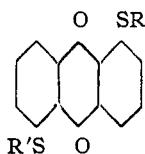
Aniline, o- and p-Toluidine Salts.—These salts were made by adding the corresponding hydrochlorides to the hot, saturated solutions of the sodium salts. All of them are very insoluble and precipitate. They were purified by extraction with hot water. They all separate as fine yellow needles which melt with decomposition at from 250° to 300°. These temperatures are not sharp enough for characterization as had been hoped. The *o*-toluidine salts decompose at lower temperatures than the aniline or *p*-toluidine.

TABLE VII.

ANILINE, *o*-TOLUIDINE AND *p*-TOLUIDINE SALTS. 1,5-RS.C₁₄H₉O₂.SO₃H₃NAr.

Alkyl.	Base.	Decomp. temp. °C.	Sulfur.	
			Calc. %.	Found. %.
Methyl	Aniline	290-299	15.00	14.70
	<i>o</i> -Toluidine	285-290	14.53	14.75
	<i>p</i> -Toluidine	298-304	14.53	14.50
Ethyl	Aniline	276-285	14.53	14.30
	<i>o</i> -Toluidine	264-274	14.08	14.10
	<i>p</i> -Toluidine	276-285	14.08	14.25
Propyl	Aniline	270-277	14.08	14.15
	<i>o</i> -Toluidine	255-257	13.66	13.75
	<i>p</i> -Toluidine	13.66	13.85
Butyl	Aniline	257-259	13.66	13.80
	<i>o</i> -Toluidine	234-237	13.26	13.35
	<i>p</i> -Toluidine	256-260	13.26	13.10
<i>iso</i> -Amyl	Aniline	263-265	13.26	13.10
	<i>o</i> -Toluidine	250-254	12.89	12.80
	<i>p</i> -Toluidine	267-277	12.89	12.90

V. 1,5-Anthraquinone Dialkyl Dithio-ethers.



When the two alkyl groups are the same, these may be obtained directly by heating the sodium 1,5-disulfonate with excess of alkali and mercaptan for a long time. They are always formed to a greater or less extent in the preparation of the intermediate thio-ether sulfonates described above and are obtained by extraction of the crude products with benzene. The diethyl and dibutyl compounds were obtained in this way.

The intermediate monosulfonate may be isolated and purified and the second alkyl group, which may be the same as the first or different, introduced. Of course the mixed thio-ethers must be prepared in this way.

The alkyl thio-ether sodium sulfonate is suspended in about 100 parts of water, containing an excess of caustic soda with the mercaptan, and the mixture boiled. The reaction is slow on account of the low solubility of the sodium salts, particularly of those containing the higher alkyl groups. It is best to introduce the lower alkyl group first. The resulting dithio-ethers are extracted with hot benzene and recrystallized from benzene, or alcohol, or mixtures of the two. The details of the various preparations are given in tabular form.

TABLE VIII.

PREPARATION OF 1,5-ANTHRAQUINONE DIALKYL DITHIO-ETHERS.							
First alkyl.	Alkyl introduced.	Wt. sulfonate. G.	Vol. water. Cc.	Caustic soda. G.	Wt. RSH. G.	Time. Hours.	Yield. G.
Methyl	Methyl	5	500	2	gas	4	4
	Ethyl	10	500	4	gas	4	1
	Propyl	8	500	2	6	23	5
	Butyl	8	500	2	4.6	22	5
Ethyl	<i>iso</i> -Amyl	8	500	2	4.4	6	6
	Propyl	5	350	2	5	30	4
	Butyl	5	350	2	5	30	4
Propyl	<i>iso</i> -Amyl	5	300	2	5	12	4.5
	Propyl	10	750	2	6	20	7
	Butyl	8	750	2	6	7	3
<i>iso</i> -Amyl	Butyl	10	1000	2	5	41	6.5
	<i>iso</i> -Amyl	10	300	2	5	11	2.5

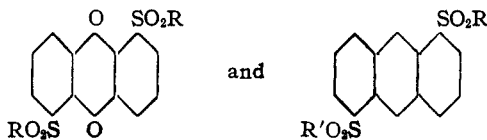
TABLE IX.

PROPERTIES AND ANALYSES OF 1,5-ANTHRAQUINONE DIALKYL DITHIO-ETHERS. 1,5-C₁₄H₈O₂(SR)₂ AND 1,5-RS.C₁₄H₈O₂.SR'.
Sulfur.

Alkyls.	M. p. °C.	Calc. %.	Found. %.	Color and form.	
Methyl	Methyl	Chars.	21.35	21.03	red needles
	Ethyl	229	20.40	20.35	yellow needles
	Propyl	209	19.53	19.45	orange needles
	Butyl	173.5	18.73	18.50	yellow needles
Ethyl	<i>iso</i> -Amyl	175	17.99	17.90	orange-yel. leaflets
	Ethyl	226.5	19.53	19.40	orange grains
	Propyl	188.5	18.73	18.65	orange grains
	Butyl	156	17.99	17.75	red crystals
Propyl	<i>iso</i> -Amyl	152	17.31	17.25	gold-yellow plates
	Propyl	227	17.99	18.30	orange cryst. powder
	Butyl	175	17.31	16.95	orange prisms
Butyl	Butyl	159.5	16.68	16.65	yellow needles
	<i>iso</i> -Amyl	134	16.09	15.80	orange needles
Di- <i>iso</i> -amyl	158.5	15.55	15.59	yellow needles	

Comparing these, we see that the dimethyl compound has the highest melting point and that the melting point is progressively lowered as heavier alkyl groups are substituted for one of the methyls. Gattermann gives the diethyl thio-ether as melting at 230°.

VI. 1,5-Anthraquinone Dialkyl Disulfones.



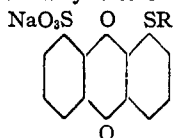
These were prepared just as were the monosulfones by oxidizing the dithio-ethers with fuming nitric acid. They separate as faintly yellow crystalline powders, when their nitric acid solutions are-poured into hot water. They are very slightly soluble in most solvents.

TABLE X.

PROPERTIES AND ANALYSES OF 1,5-ANTHRAQUINONE DIALKYL DISULFONES, 1,5-C₁₄H₈O₂-(SO₂R)₂ AND 1,5-R'SO₂.C₁₄H₈O₂.SO₂R.

Alkyls.		M. p. °C.	Sulfur.		Form.
			Calc. %.	Found. %.	
Methyl	Methyl	chars.	17.60	17.53	powder
	Ethyl	> 300	16.95	16.90	fine needles
	Propyl	291	16.34	16.50	crystalline grains
	Butyl	264	15.78	15.75	crystalline grains
Ethyl	<i>iso</i> -Amyl	266	15.25	15.00	crystalline grains
	Ethyl	269.5	16.34	16.40	fine needles
	Propyl	243.5	15.78	15.65	fine needles
	Butyl	194	15.25	15.45	powder
Propyl	<i>iso</i> -Amyl	198	14.76	14.80	powder
	Propyl	265	15.25	15.15	fine needles
	Butyl	220	14.76	14.95	crystalline grains
Butyl	Butyl	184.5	14.30	14.10	crystalline powder
	<i>iso</i> -Amyl	203.5	13.87	14.00	crystalline powder
<i>iso</i> -Amyl	<i>iso</i> -Amyl	202	13.46	13.50	powder

VII. Anthraquinone-1-alkyl-thio-ether-8-sulfonic Acids.



These can be prepared just as the corresponding 1,5 compounds except that it is much more difficult to isolate the sodium salts as, on account of their greater solubility, they react readily with a second molecule of the mercaptan to give the disulfides. In an experiment in which 50 g. of sodium anthraquinone-1-8-disulfonate, 800 cc. of water, 13 g. of caustic soda and 37 g. of butyl mercaptan were heated for 24 hours at 100°, 20 g. or 55% of the dithio-ether was formed.

The details of a number of preparations are given in tabular form.

TABLE XI.

PREPARATION OF SODIUM ANTHRAQUINONE-1-ALKYL-THIO-ETHER-8-SULFONATES.

Alkyl.	1,8-RS.C ₁₄ H ₈ O ₂ .SO ₃ Na.H ₂ O.					
	Sulfonate. G.	Water. Cc.	NaOH. G.	RSH. G.	Time. Hrs.	Yield. %.
Methyl	82	500	25	gas	2	57
Ethyl	82	500	25	gas	3	45
Propyl	82	500	8	36	3	21
Butyl	82	500	8	24	2	30
<i>iso</i> -Amyl	82	500	10	28	4	50

TABLE XII.

PROPERTIES AND ANALYSES OF SODIUM SALTS. 1,8-RS.C₁₄H₈O₂.SO₃Na.H₂O.

Alkyl.	Water.		Sodium.		Color and form.
	Calc. %.	Found. %.	Calc. %.	Found. %.	
Methyl	4.81	4.84	6.45	6.60	brick-red cryst.
Ethyl	6.21	6.11	orange needles
Propyl	2.29	2.26	5.98	6.23	ochre-yellow, m. p. 289°
Butyl	4.33	4.39	5.77	5.59	orange-yellow needles
<i>iso</i> -Amyl	4.19	4.16	5.58	5.34	brownish-orange needles

The ethyl compound is anhydrous and the propyl contains only one-half molecule of water.

TABLE XIII.

PROPERTIES AND ANALYSES OF BARIUM SALTS. 1,8-(RSC₁₄H₆O₂SO₃)₂Ba.

Alkyl.	Barium.		Color and form.
	Calc. %.	Found. %.	
Methyl	17.09	16.73	brick-red cryst. powder
Ethyl	16.51	16.31	orange needles
Propyl	15.97	16.08	orange powder
Butyl	15.47	15.12	orange needles
<i>iso</i> -Amyl	14.99	14.80	brownish-orange needles

TABLE XIV.

OTHER SALTS OF ANTHRAQUINONE-1-BUTYL-THIO-ETHER-8-SULFONIC ACID. 1,8-(C₄H₉-SC₁₄H₆O₂SO₃)₂Mⁿ.

Base.	Water of hydration.	Water.		Metal.		Color and form.
		Calc. %.	Found. %.	Calc. %.	Found. %.	
Strontium	10.45	10.63	orange-red powder
Calcium	4 H ₂ O	8.35	7.87	5.07	5.10	red cryst. powder
Lead	21.63	21.69	orange-red powder
Nickel	α H ₂ O	7.25	7.08	orange-red needles
Cobalt	α H ₂ O	7.28	7.40	orange-red needles
Copper	3 H ₂ O	3.21	3.40	7.81	7.85	ochre-yellow needles

The nickel and cobalt salts contain water, but it was not determined.

The sodium butyl compound dyes unmordanted wool much as does the corresponding 1,5 salt but the shades obtained were dull and unattractive.

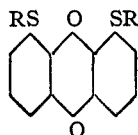
Aniline, o- and p-Toluidine Salts.—These were made by precipitation as in the other series. All of them come down as fine needles with colors varying from yellow to orange.

TABLE XV.

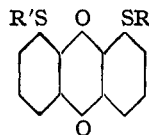
ANILINE, *o*-TOLUIDINE AND *p*-TOLUIDINE SALTS. 1,8-RS.C₁₄H₆O₂.SO₃H₂NAR.

Alkyl.	Base.	Decomp. Temp. °C.	Sulfur.		Color.
			Calc. %.	Found. %.	
Methyl	Aniline	260	15.00	14.85	orange
	<i>o</i> -Toluidine	255	14.53	14.30	yellow
	<i>p</i> -Toluidine	260	14.53	14.37	orange
Ethyl	Aniline	250	14.08	14.01	orange
	<i>o</i> -Toluidine	260	13.66	13.64	yellow
	<i>p</i> -Toluidine	255	13.66	13.56	orange
Propyl	Aniline	242	13.66	13.85	yellow
	<i>o</i> -Toluidine	260	13.26	13.60	yellow
	<i>p</i> -Toluidine	260	13.26	13.50	yellow
Butyl	Aniline	260	13.26	13.47	orange
	<i>o</i> -Toluidine	260	12.89	13.06	orange
	<i>p</i> -Toluidine	255	12.89	12.98	orange

VIII. 1,8-Anthraquinone Dialkyl Dithio-ethers.



and



The compounds in which the two alkyls are the same are readily obtained directly from the sodium 1,8-disulfonate. Those described below were obtained in this way as by-products in the preparation of the monosulfonates described above. The mixed compounds were prepared as were the corresponding 1,5 compounds. The details are given in tabular form.

TABLE XVI.

PREPARATION OF 1,8-ANTHRAQUINONE DIALKYL DITHIO-ETHERS.							
Original alkyl.	Alkyl introduced.	Sulfonate. G.	Water. Cc.	NaOH. G.	RSH. G.	Time. Hours.	Yield. G.
Methyl	Ethyl	6	300	1	gas	3	3.5
	Propyl	6	300	1	2	3	5
	Butyl	6	250	1	2	3	4
	<i>iso</i> -Amyl	7	200	1	2	3	3.5
Propyl	<i>iso</i> -Amyl	7	250	1	2	4	4
Butyl	Ethyl	10	50	1	5	3	3
	Propyl	5	50	1	2	6	5
	<i>iso</i> -Amyl	7	250	1	2	3	4
	<i>iso</i> -Amyl	7	300	1	2	3	4

TABLE XVII.

PROPERTIES AND ANALYSES OF 1,8-ANTHRAQUINONE DIALKYL DITHIO-ETHERS.
1,8-C₁₄H₆O₂(SR)₂ AND 1,8-R'S.C₁₄H₆O₂.SR.

Alkyl.		M. p. °C.	Sulfur.		Color and form.
			Calc. %.	Found. %.	
Methyl	Methyl	222	21.35	21.11	brownish-yellow needles
	Ethyl	210	20.40	20.45	red crystals
	Propyl	173.5	19.53	19.60	orange-red needles
	Butyl	134	18.73	18.74	orange needles
	<i>iso</i> -Amyl	114	17.99	18.10	fine orange needles
Ethyl	Ethyl	167.5	19.53	19.44	red crystals
	Butyl	95	17.99	18.14	orange-yellow needles
Propyl	Propyl	142	17.99	17.87	brick-red prisms
	Butyl	119.5	17.31	17.20	orange needles
	<i>iso</i> -Amyl	104	16.68	16.58	orange powder
Butyl	Butyl	131	16.68	16.67	red needles
	<i>iso</i> -Butyl	103.5	16.68	16.70	orange prisms
	<i>iso</i> -Amyl	116.5	16.09	16.21	orange crystals
Di- <i>iso</i> -amyl		133	15.55	15.27	long orange plates

IX. 1,8-Anthraquinone Dialkyl Disulfones.



These sulfones are readily obtained by oxidation of the thio-ethers with fuming nitric acid. They are all very slightly yellow crystalline powders.

TABLE XVIII.

PROPERTIES AND ANALYSES OF 1,8-ANTHRAQUINONE DIALKYL DISULFONES.
1,8-C₁₄H₆O₂(SO₂R)₂ AND 1,8-R'SO₂.C₁₄H₆O₂.SO₂R.

Alkyl.		M. p. °C.	Sulfur.	
			Calc. %.	Found. %.
Methyl	Methyl	310	17.60	17.35
	Ethyl	220	16.95	16.79
	Propyl	211	16.34	16.38

TABLE VIII (continued).

Alkyl.		M. p. °C.	Calc. %.	Sulfur.	
				Found. %.	
Ethyl	Butyl	169	15.78	15.38	
	<i>iso</i> -Amyl	172	15.25	15.09	
	Ethyl	228	16.34	16.26	
	Butyl	128	15.25	15.45	
Propyl	Propyl	210	15.25	14.80	
	Butyl	200.5	14.76	14.70	
	<i>iso</i> -Amyl	147.5	14.30	13.95	
Butyl	Butyl	138	14.30	14.00	
	<i>iso</i> -Butyl	168.5	14.30	13.95	
	<i>iso</i> -Amyl	154	13.87	13.94	
Di- <i>iso</i> -amyl		176	13.46	13.40	

Summary.

It has been found that by heating the sodium salt of α -anthraquinone sulfonic acid with a mercaptan in presence of caustic soda, the sulfonic acid group is readily replaced yielding an anthraquinone alkyl thio-ether, $C_{14}H_7O_2SR$. When two α -sulfonic acid groups are present these are replaced in succession, yielding first alkyl thio-ether sulfonic acids, 1,5- and 1,8- $NaO_3S.C_{14}H_6O_2.SR$ and then dialkyl dithio-ethers, 1,5- and 1,8- $R'S.C_{14}H_6O_2.SR$. A large number of compounds have been prepared in which R is methyl, ethyl, propyl, butyl, *isobutyl* and *iso*-amyl.

BALTIMORE, MARYLAND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS,
NORTHWESTERN UNIVERSITY.]

ARSENATED BENZOPHENONE AND ITS DERIVATIVES.¹

By W. LEE LEWIS AND H. C. CHEETHAM.

Received June 11, 1921.

Introduction.

Arsenic in an aromatic nucleus does not interfere with many typical organic reactions. The Friedel and Crafts reaction, however, has found but limited² application in organic arsenical chemistry. With a view to determining whether arsenated benzoyl chloride would enter into the Friedel and Crafts reaction, thus yielding a new type of arsenic compound of possible therapeutic value,³ the work described in this paper was undertaken.

¹ This work was done under a grant from the Interdepartmental Hygiene Board, Washington, D. C., Dr. T. A. Storey, Sec'y.

² Lewis, Lowry and Bergeim, *THIS JOURNAL*, **43**, 892 (1921).

³ Therapeutic tests upon new compounds developed under this grant are being conducted by Dr. A. S. Loevenhart, Department of Pharmacology, University of Wisconsin.