[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, YALE SCHOOL OF MEDICINE]

# The Synthesis of a Disulfenic Acid. Anthraquinone-1,4-disulfenic Acid

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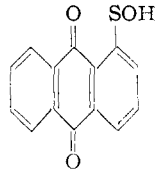
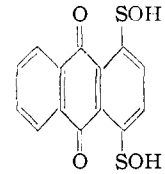
The synthesis of anthraquinone-1,4-disulfenic acid (II) is described. This compound represents the first disulfenic acid and the second sulfenic acid to be isolated.

Sulfenic acids, generally designated as RSOH, may be considered as the parent compounds of the sulfenyl thiocyanates (RSSCN), sulfenyl halides (RSCl), sulfenic acid esters (RSOR') and the sulfenamides ($RSNR_2'$). They have been suggested to be hydrolytic scission products of disulfides[1-5] and S-arylthiosulfuric acids,[6] while certain sulfenic acids have been proposed as intermediates in the chemical or metabolic oxidation of thiols,[7] participants in the photosynthetic processes of plants[1,8] and as possible intermediates in the oxidation of proteins.[9] However, with the single exception of the isolation of 1-anthraquinonesulfenic acid (I) in 1912,[10] all attempts to isolate other sulfenic acids in the anthraquinone, benzene or aliphatic series have been unsuccessful.[1,11-19] In this paper, we describe the synthesis of the corresponding disulfenic acid (II) and discuss the possible significance of this in terms of the structural requirements for the stabilization of the sulfenic acid group.




I




II

The synthetic sequence leading to II, as well as the conversions effected in the present study, are summarized in Fig. 1. The potassium salt of 1-anthraquinonesulfonic acid (III) was converted to 1-chloroanthraquinone by the procedures of Scott and Allen.[20] Nitration of 1-chloroanthraquinone according to the method of Eckert and Steiner[21] yielded IV. Treatment of IV at reflux with sodium disulfide, in aqueous dioxane, yielded a brick-red, high melting, nitrogen-free substance whose structure has been established as that of V. In the preparation of V, if solvent conditions other than those specified were used, various mixtures were obtained whose color and composition depended upon the time of reflux, solvent, stoichiometry, etc. The polymeric disulfide V is insoluble in all solvents investigated and, therefore, could not be freed of the usual impurities accompanying reactions of this nature. The structure of V was established by conversion to anthraquinone-1,4-disulfonic acid (IX), a previously reported compound.[22] The disulfonic acid was then converted to the also known 1,4-dichloroanthraquinone (X) which, in turn, was reconverted to V by the same procedures employed for the sequence IV → V. The polymeric disulfide, prepared in this manner, was of lighter color but otherwise identical in its reactions and high decomposition point (> 360°) to that prepared from IV. Conversion of IV to V involves replacement of a nitro group (situated *ortho* to a strong electron attracting substituent) by a nucleophilic agent. Reactions of this type are well known and the use of $S^-$ as the nucleophile has been reported previously.[23]

Chlorinolysis of V, under anhydrous conditions, employing aluminum chloride (formed *in situ*) catalysis,[24] gave 1,4-anthraquinonedisulfenyl chloride (VI) as balls of red needles from benzene. Treatment of VI with anhydrous methanol in benzene (trace of pyridine)[25] yielded dimethylanthraquinone-1,4-disulfenate (VII), which crystallized as red, glistening needles from benzene and methanol. When either VII or VI were treated with boiling morpholine, the same dimorpholide (VIII) was obtained. Compounds VI and VIII are stable when pure. The dimethyl ester VII is particularly stable and no precautions are required for its storage. Compounds VI, VII, VIII and, as previously noted V, were all converted in high yield to IX by oxidation with moist chlorine.

Fries[10] accomplished the synthesis of 1-anthraquinonesulfenic acid (I) by hydrolyzing the corresponding methyl sulfenate with strong potassium hydroxide solution, followed by the liberation of the free sulfenic acid with acetic acid. The hydrolysis of VII to 1,4-anthraquinonedisulfenic acid (II) was carried out similarly and, for comparative purposes, the hydrolysis of methyl 1-anthra-

(1) M. Calvin, *et al.*, THIS JOURNAL, **76**, 1760, 4348 (1954).
(2) W. G. Prescott and S. Smiles, *J. Chem. Soc.*, **99**, 640 (1911).
(3) A. Schöberl, *Ber.*, **70**, 1186 (1937).
(4) A. Schöberl and T. Hornung, *Ann.*, **534**, 210 (1938).
(5) J. E. Roth, *J. Biol. Chem.*, **126**, 147 (1938); **130**, 297 (1939).
(6) H. Z. Lecher, *J. Org. Chem.*, **20**, 475 (1955).
(7) N. W. Pirie, *Biochem. J.*, **28**, 305 (1934); G. Medes and N. Floyde, *J. Org. Chem.*, **36**, 259 (1942); R. E. Basford and F. M. Huennekens, THIS JOURNAL, **77**, 3837 (1955); G. Toennies, *J. Biol. Chem.*, **122**, 27 (1937).
(8) D. F. Bradley and M. Calvin, *Arch. Biochem. Biophys.*, **53**, 99 (1954).
(9) H. Fraenkel-Conrat, *J. Biol. Chem.*, **217**, 373 (1955).
(10) K. Fries, *Ber.*, **45**, 2965 (1912).
(11) K. Fries and G. Schurmann, *ibid.*, **52**, 2170 (1919).
(12) K. Fries and G. Schurmann, *ibid.*, **52**, 2182 (1919).
(13) T. Zincke and K. Eismayer, *ibid.*, **51**, 751 (1918).
(14) T. Zincke and J. Baeumer, *Ann.*, **416**, 86 (1918).
(15) T. Zincke and F. Farr, *ibid.*, **391**, 55 (1912).
(16) T. Zincke and S. Lenhardt, *ibid.*, **400**, 1 (1913).
(17) T. Zincke and H. Rose, *ibid.*, **406**, 103 (1914).
(18) N. Kharasch and T. C. Bruice, THIS JOURNAL, **73**, 3240 (1951).
(19) N. Kharasch, W. King and T. C. Bruice, *ibid.*, **77**, 931 (1955).
(20) W. J. Scott and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 128.
(21) A. Eckert and K. Steiner, *Monatsh.*, **35**, 1138 (1914).
(22) V. V. Kozlov, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 289 (1947).
(23) See, for example, O. Foss, *Acta Chem. Scand.*, **1**, 307 (1947).
(24) N. Kharasch, G. I. Gleason and C. M. Buess, THIS JOURNAL, **72**, 1796 (1950).
(25) L. Goodman and N. Kharasch, *ibid.*, **77**, 6541 (1955).

quinonesulfenate to I was repeated.[26] A comparison of the observations on the hydrolysis and products formed from methyl 1-anthraquinonesulfenate and VII are recorded in Table I.

TABLE I

COMPARATIVE OBSERVATIONS ON 1-ANTHRAQUINONESULFENIC ACID AND 1,4-ANTHRAQUINONEDISULFENIC ACID

| | I | II |
|---|---|---|
| Methyl esters in ethanol | Yellow | Red |
| Dil. ethanolic soln. of free acids | Orange | Magenta |
| Aqueous soln. of potassium salts | Blue | Blue |
| Acetone soln. of potassium salts | Green | Green |
| Lead salts | Blk. ppt. | Blk. ppt. |
| Barium salts | Green | Green |
| Dil. aq. acetone soln. of barium salts | Blue | Blue |
| Crystalline form of acid from acetone–water | Red microscopic needles | Purple microscopic needles |
| Color change on heating above 100° | Red → Yellow | Purple → Brick-red |

Though II was found to be stable to desiccation (see following discussion) attempts at recrystallization were always accompanied by the formation of small quantities of bright red alkali-insoluble material, which prevented the preparation of a suitable analytical sample. As expected, also, the product presumed to be the disulfenic acid (II) was readily oxidizable. Thus, in dilute methanolic solution, the characteristic purple color persisted for about a week, slowly changing to a pale yellow; and, in dilute base, the blue color of the potassium salt persisted for many weeks before fading, if the solution was kept in the dark and free of air. However, either the potassium salt or the free acid were immediately destroyed if their alcohol solutions were shaken with activated carbon (Norite). When treated with moist chlorine, II was converted to IX.

The strongest evidence for the proposed structure for II was obtained by converting the purple acid to the dimethyl sulfenate (VII). When II was treated with anhydrous hydrogen chloride in an inert solvent, followed by solution in absolute methanol, the methyl ester VII could be regenerated in 47–55% over-all yield from II. This conversion of the purple acid to the methyl sulfenate, *via* the sulfenyl chloride (VI), corresponds to the like reactions of I,[10] and we interpret this as unequivocal evidence that the oxidation state of the purple acid is at the sulfenic acid level. The stability of II, in the dry state and in the absence of air, was confirmed by the finding that weeks after its isolation it could be converted to the methyl sulfenate in yields corresponding to those obtained when freshly prepared acid was employed. Simply treating II with methanol did not yield VII.

The barium salt of II was obtained by treatment of either the free disulfenic acid or its dimethyl ester with barium hydroxide. When carbon dioxide was passed through a dilute aqueous ethanol solution of either the barium or potassium salt of II, the blue color faded to the red of the sulfenic acid. The sodium salt, but not the barium salt, could then be regenerated by removing excess carbon dioxide *in vacuo*. This would tend to place the first ionization constant of II at between $10^{-6}$ and $10^{-12}$. The black amorphous lead salt of II was prepared easily by adding an acetone solution of II to an aqueous solution containing excess lead acetate. The lead salt was insoluble in water and all neutral organic solvents but dissolved readily if a suspension of the salt in aqueous ethanol was acidified with acetic acid, to yield the color of the free sulfenic acid, or when the solution is made alkaline with potassium hydroxide, to yield the blue color of the potassium salt.

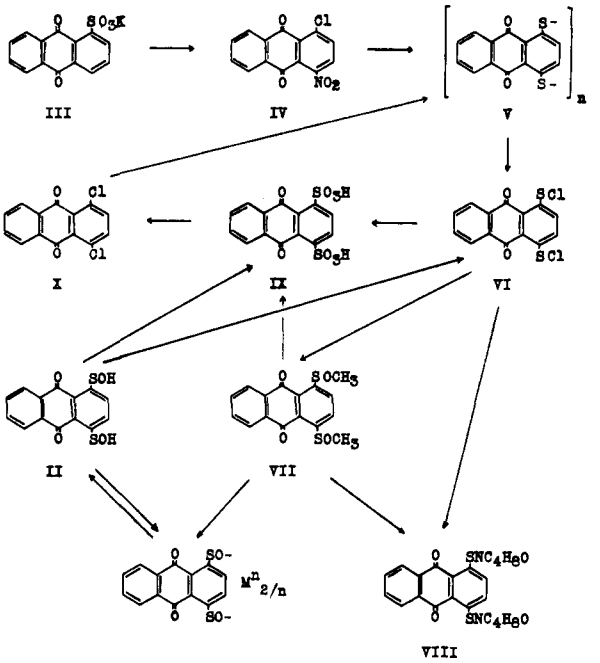



Fig. 1.

The reason for the stabilities of I and II, at least so far as to permit their isolation, as contrasted to the complete instability of 2-anthraquinonesulfenic acid[11] (XI) and 4-amino-1-anthraquinonesulfenic acid (XII)[12] as well as the apparent non-existence of 1-fluorenonesulfenic acid (XIII),[18] is not evident. Stabilization through hydrogen bonding of the acid hydrogen to the carbonyl group of anthraquinone,[27] or interaction of the sulfur with the carbonyl oxygen,[6] do not appear to offer a complete explanation, since XII and XIII are not so stabilized. It appears reasonable to suppose that, in addition to the interaction of the sulfenic acid group with the carbonyl oxygen of anthraquinone, there is required for the stabilization of the sulfenic acid grouping its attachment to a highly electronegative carbon atom.[28] Employing such a dual prerequisite for the stabilization of the SOH group, the instability of XI would be explained on the basis of the inability of SOH to interact with the carbonyl group, while for XII and

(26) The original work of Fries has been confirmed previously by A. T. Fowler (see footnote 12 of ref. 18) and by W. Jenny, *Helv. Chim. Acta*, **35**, 845 (1952).

(27) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 276 (1946).

(28) Similar reasoning can be used in the case of the selenenic acids, where *o*-nitro or *o*-keto groups apparently are required for stability (see ref. 27). Sulfenic acids are not stabilized by *o*-nitro groups, in part due to the intermolecular oxidation of the sulfenic acid moiety and reduction of the nitro group to yield aminosulfonic acids (see ref. 19).

XIII instability could be ascribed to the decreased positive nature of the 1-position as compared to anthraquinone. This may be a logical argument, since it is certain that a *p*-amino group would lower the positive character or the 1-position of anthraquinone and the fluorenone nucleus is known to be not as electron deficient as that of anthraquinone.[29]

Since II is less stable than I but of greater stability than XII, the above reasoning suggests that the *p*-SOH group is electron releasing but not to such a degree as the *p*-amino group. From the known properties of the *p*-sulfhydryl and *p*-hydroxyl groups, this would appear to be a logical supposition. Semi-quantitatively, the electron releasing characteristics of the $-SOH$ and $-SOCH_3$ groups may be determined through their effect on the visible absorption spectra of anthraquinone. A comparison of the visible spectra of I and II and their esters with those of other anthraquinones substituted in the 1- and 1,4-position is given in Table II.[30] The order of increasing values of *e* for the monosubstituted compounds may be seen to be $NH_2 > SOCH_3 = OH > OCH_3 > SOH > CH_3 > Cl > CN > NO_2$ suggesting that the SOH group is but weakly electron releasing whereas the $SOCH_3$ group has about the same electronic characteristics as a hydroxyl group. For the 1,4-disubstituted compounds the ability of the $SOCH_3$ and SOH radicals to release electrons to the anthraquinone nucleus would appear not to be that of the amino group, since, although the spectrum of VII is characterized by two bands in the visible, they are considerably hypsochromic to those of 1,4-diaminoanthraquinone and the value of *e* for VII is not twice that of I. As in the monosubstituted compounds the $SOCH_3$ group would appear to be a stronger electron repelling group than the SOH group. Thus, the spectrum of II is characterized by only one peak in the visible, and the value of *e* for II is smaller than that for VII.

On the basis of spectral evidence alone, it would appear that in accordance with the hypothesis presented above, the 1- and 4-positions of II are more positive than the 1-position of XII but less positive than the 1-position of I. As an extension of the present work, a study of the stabilities of a series of anthraquinone-1-sulfenic acids substituted with various groups in the 4-position is desirable as a further test of the hypothesis.

(29) H. Adkins, R. M. Elofson, A. G. Rossow and C. C. Robinson, THIS JOURNAL, **71**, 3622 (1949).

(30) R. H. Peters and H. H. Summers (*J. Chem. Soc.*, 2101 (1953)) consider the position of the visible band of anthraquinone to be predictably related to the electronic properties of the substituent in the 1-position. It appears to us that a better correlation is obtained by considering the molar extinction coefficients. Thus, for substituents in the 1-position the order of increasing bathochromic effect is: $-NH_2 > Cl = CN = CH_3 > OH > OCH_3 > NO_2$, while the increase in the molar extinction follows the more reasonable order $NH_2 > OH > OCH_3 > CH_3 > Cl > CN > NO_2$. The arguments presented herein on the electronic characteristics of the SOH and $SOCH_3$ groups remain the same regardless of whether the position of the bands or the molar extinctions are considered. Peters and Summers (ref. 30) point out that, in the case of the substitution of identical, strongly electron releasing groups in the 1- and 4-positions of anthraquinone, two peaks are noted in the visible region with a molar extinction coefficient twice that observed for the similarly monosubstituted compound.

TABLE II

A COMPARISON OF THE VISIBLE SPECTRA OF SULFENIC ACIDS AND THEIR ESTERS TO THOSE OF OTHER ANTHRAQUINONES

| Substituents | $\lambda_{max}$ | *e* |
|---|---|---|
| Hydrogen[a] | 410 | 60 |
| 1-$NO_2$[a] | .. | ... |
| 1-CN[a] | 417 | 70 |
| 1-Cl[a] | 415 | 100 |
| 1-$CH_3$[a] | 415 | 150 |
| 1-$OCH_3$[a] | 378 | 5,200 |
| 1-OH[a] | 402 | 5,500 |
| 1-SOH[b] | 460 | 4,700 |
| 1-$SOCH_3$[b] | 455 | 5,500 |
| 1-$NH_2$[a] | 475 | 6,300 |
| 1,4-$(SOH)_2$[c] | 524 | 5,100 |
| 1,4-$(SOCH_3)_2$[b] | 520 | 6,400 |
| | 545 | 7,000 |
| 1,4-$(NH_2)_2$[a] | 596 | 13,800 |
| | 554 | 13,400 |

[a] Data of Peters and Summers, see footnote 30; solvent methanol. [b] Solvent chloroform. [c] Solvent acetone.

## Experimental

**Poly-1,4-dithioanthraquinone (V).**—1-Chloro-4-nitroanthraquinone (IV) was recrystallized several times from chlorobenzene and then from equal volumes of hot dioxane and ethyl acetate, m.p. 262° (lit.[20] 259°). The so purified IV (4.40 g., 0.0153 mole) was suspended in 400 ml. of a good grade of dioxane (Fisher Certified) to which was added 0.512 g. (0.0157 mole) of sulfur. The solution was brought to a boil when 3.84 g. (0.0238 mole) of sodium sulfide nonahydrate dissolved in 80 ml. of dioxane and 160 ml. of water was added. The reaction mixture was heated under reflux for 5 hr. when the amorphous, brick-red precipitate of V was immediately collected and washed with large quantities of hot dioxane, water and acetone and dried at 80° (3.2 g., 77%), m.p. > 350°.

Because V was completely insoluble in all solvents, it could not be freed from silicate and other contaminants, and analyses were not performed. The compound was identified, however, in the manner given under preparation of IX and X.

**1,4-Anthraquinone Disulfenyl Chloride (VI).**—V (2 g., 0.0074 mole) was suspended in 100 ml. of chloroform in a flask fitted with side arm, gas inlet tube and condenser for downward distillation. One-half of the solvent was removed by distillation and a small piece of clean aluminum foil added. Into the cooled solution there was passed a stream of dry chlorine. After 3 hr., the flask was tightly stoppered and set aside at room temperature for at least 12 hr. After refrigeration for an additional several hours, the product was collected, washed with dry ether and the small pieces of unreacted aluminum picked out. The product (2.2 g., 87.5%) was used without further purification in the preparation of VII, VIII and IX.

For analysis the sulfenyl halide was recrystallized to constant melting point from anhydrous benzene and dried at 130° over $P_2O_5$ at 1 mm., m.p. 270°.

*Anal.* Calcd. for $C_{14}H_6S_2Cl_2O_2$: C, 49.4; H, 1.77; S, 18.8. Found: C, 49.57; H, 2.01; S, 18.15.

**Dimethyl 1,4-Anthraquinonedisulfenate (VII).**—Two grams (0.0059 mole) of VI was suspended in 250 ml. of absolute methanol, and there was then added 150 ml. of anhydrous benzene and 1 ml. of dry pyridine. The mixture was then brought to a boil when all but a trace of the solid material dissolved. The flask containing the reaction mixture was tightly stoppered and set aside for two days.

The reaction mixture was brought to a boil for a few minutes, a small amount of activated carbon (Norite) added, boiling continued for 5 min. when the red solution was filtered and concentrated to one-half volume. After several hours, long red needles begin to form. At this time the reaction mixture was chilled for 12 hr. and the product collected. In this manner there was obtained 1.0 g. (51%) of VII, m.p. 176–179°. For analysis the product was recrystallized several times from a mixture of benzene and

methanol and dried at 100° for 2 hr. over $P_2O_5$ at 1.0 mm., m.p. 189–190°.

*Anal.* Calcd. for $C_{16}H_{12}O_4S_2$: C, 57.81; H, 3.64; S, 19.30. Found: C, 58.1; H, 3.81; S, 19.45.

**1,4-Anthraquinonedisulfenyl Morpholide (VIII).**—Either VI or VII when boiled for a short time in a small volume of morpholine dissolves, and on cooling, red-brown needles of the dimorpholide are deposited. After collecting and washing with hot ethanol and benzene the product was found to sinter at 271° and not to melt below 300°, though decomposition was complete. For analysis the compound was recrystallized from pyridine (charcoal) several times (melting characteristic unchanged) and dried at 100° for 12 hr. over $P_2O_5$ at 1.0 mm.

*Anal.* Calcd. for $C_{22}H_{22}O_4S_2N_2$: C, 59.9; H, 5.01; N, 6.34; S, 14.49. Found: C, 59.91; H, 5.21; N, 6.33; S, 14.14.

**1,4-Anthraquinonedisulfenic Acid (II).**—The disulfenate ester VII (0.5 g., 0.0015 mole) was suspended in 20 ml. of absolute ethanol which was brought to a boil and 1.0 ml. of 33% aqueous potassium hydroxide (0.006 mole) added. Boiling was continued for 4 min. when 100 ml. of hot distilled water was added. The resultant clear blue solution was then quickly chilled, filtered and the filtrate made weakly acid with acetic acid. The purple coagulant was collected and washed with a large quantity of cold water. The moist precipitate was then taken up in cold acetone, the deep magenta solution filtered, and to the filtrate there was added water until the solution became just slightly cloudy. The solution was then refrigerated and water added very gradually until precipitation was completed. In this manner the acid II was obtained as purple microscopic needles (0.1 to 0.12 g., 22–26%). When heated above 100° II turned from purple to yellow.

Additional recrystallizations from acetone always resulted in the formation of small amounts of alkali-insoluble material. No other solvent was found that was better for recrystallization than acetone and an analytical sample could not be prepared.

**The Stability of II and the Conversion of II to VII.**—Anhydrous chloroform (100 ml.) previously saturated with dry hydrogen chloride at 0° was added to 118 mg. (0.00039 mole) of dry II and the reaction mixture allowed to set at 0° for 12 hr. All the solvent was then aspirated off, and to the dry residue there was added 100 ml. of anhydrous methanol and 1 ml. of dry pyridine. The flask was then warmed to a boil and set aside for 12 hr. The methanolic supernatant solution was decanted and the residue taken up in 50 ml. of hot, anhydrous benzene. The benzene and methanolic solutions were then combined and allowed to cool. After a few hr. the precipitation of a high melting amorphous material (*ca.* 40 mg.) was complete. This substance was removed and the filtrate concentrated to 100 ml. and set aside. The characteristic crystals of the diester soon appeared. These were collected and the filtrate concentrated in turn to 50 and 25 ml., respectively, the crystalline ester being removed each time. In this fashion there was obtained a total of 60–70 mg. of VII, m.p. 176–179° (47–55% yield from II). The melting point was identical to that of VII as obtained from the reaction of VI and methanol, and on recrystallization several times from benzene and methanol the melting points were found to be between 185–188° which is very close to that of the analytical sample of VII (no mixed melting point depression with an authentic sample of VII).

This procedure was carried out on samples of the sulfenic acid prepared a month in advance with no appreciable difference in yield of VII if II were kept in a desiccator under refrigeration.

**1,4-Anthraquinonedisulfonic Acid (IX) and 1,4-Dichloroanthraquinone (X).**—The disulfonic acid IX was obtained in good yield when either V, VI, VII or II was suspended in 200 volumes of 90% aqueous acetic acid which was then saturated, in the cold, with chlorine gas. The reaction mixture was filtered and allowed to set for 10 hr. when the white to yellow needles were collected. The crude acid is best recrystallized from 90% acetic acid, m.p. 269–269.5° (lit.[21] 264–265°). The crude yield from 0.4 g. (0.0015 mole) of V was 0.41 g. or 75% of theory (m.p. 263–264°).

*Anal.* Calcd. for $C_{14}H_8O_8S_2 \cdot H_2O$: C, 43.52; H, 2.61; S, 16.60. Found: C, 43.61; H, 2.85; S, 17.47.

The disulfonic acid could be converted to 1,4-dichloroanthraquinone by the usual procedure,[20] m.p. 190° (lit.[21] 186.5°). When the dihalide, so obtained (0.531 g., 0.0019 mole), was treated in the same manner as in the preparation of V from IV, the polymeric disulfide was obtained (0.52 g., 100% yield), m.p. > 360°.

**Absorption Spectra.**—These were determined with a Model DU Beckman spectrophotometer. Extinction coefficients were calculated from spectral measurements made with $\sim 10^{-4}$ molar solutions; the maximum absorbances were all between 0.5 and 0.8. The solvents employed are as noted in Table II.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA, AND THE RESEARCH COUNCIL OF ALBERTA]

# Observations on Some Alkyl Substituted Anthracenes and Anthraquinones

BY ROBERT J. CRAWFORD, SIDNEY LEVINE, RICHARD M. ELOFSON AND REUBEN B. SANDIN

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1,2-Dimethylanthraquinone and some related alkyl substituted anthraquinones have been examined from the standpoint of polarographic and chemical reduction and controlled potential electrolysis. The effectiveness of alkyl substitution in lowering the negative potential is: $\alpha > \beta$, dimethyl > monomethyl, six-membered ring > five-membered ring and 1,2-dimethyl > six-membered ring. The $\alpha$-substituted anthraquinones show evidence of oxanthrol isomerization. It is suggested that 1,2,9,10-tetramethylanthracene behaves as a crowded molecule from the standpoint of preparation and properties.

It is known that 9,10-dihydro derivatives of 1,2-dimethylanthracene are very resistant to aromatization. For example, compound II resists demethoxylation and does not yield 1,2,9,10-tetramethylanthracene (I) even after shaking for six days with sodium powder in ether.[1] On the other hand, 9,10-dimethylanthracene is obtained in good yield from the corresponding dimethoxy compound. Again, compound III does not undergo dehydrogenation to yield I, whereas 9,10-dihydroanthracene is smoothly transformed into 9,10-dimethylanthracene with sulfur at 230°.[2]

In contrast to this behavior it is known that compound I tends to lose aromaticity and to revert to the 9,10-dihydro state. For example, I has been

(1) G. M. Badger, J. W. Cook and F. Goulden, *J. Chem. Soc.*, 16 (1940).

(2) G. M. Badger, F. Goulden and F. L. Warren, *ibid.*, 18 (1941).