

appears to be consistent with expectation based on present theory. The other exception is benzoyl-trimethylacetylstyrene, $C_6H_5COC(C_6H_5)=CH-COC(CH_3)_3$, which is *cis*⁹ and doubtless also is nonplanar with respect to the unsaturated 1,4-diketone system.

Further studies on *cis-trans* relationships in this field are in progress.

Experimental

The reductions of samples of the *cis*- and *trans*-phenyl-dibenzoylthylenes were run under conditions which were identical in all details.

(9) R. C. Downing, Dissertation, University of Virginia (1941).

A solution of 0.250 g. of the *cis*-unsaturated diketone in 10 ml. of concd. acetic acid was brought to 100° in a steam-bath. Half a gram of zinc dust was added and the mixture was stirred manually for 2 min. The mixture was filtered; the zinc residue was washed with 1 ml. of hot, and 1 ml. of cold solvent: 1.2 ml. of alcohol was added to the filtrate and water until turbidity developed; upon cooling to 0° 0.120 g. of 2,4,5-triphenylfuran was obtained; further addition of water and cooling gave an additional 0.025 g.; total yield 37.5% (61.2% from the *trans*-isomer); a third addition of water and cooling gave 0.026 g. of phenyl-dibenzoylthane and a fourth treatment gave an additional 0.030 g.; total yield 50.1% (22.3% from the *trans*-isomer). The products were practically pure and were identified by mixture melting points with authentic samples; total yield of products from *cis*, 87.6%, and from *trans*, 83.5%.

CHARLOTTESVILLE, VA.

RECEIVED JANUARY 13, 1951

[CONTRIBUTION FROM THE NAUGATUCK CHEMICAL DIVISION, UNITED STATES RUBBER COMPANY]

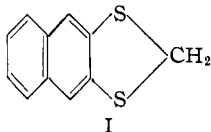
The Reaction of 2,3-Dichloro-1,4-naphthoquinone with Salts of Alkyl Substituted and Unsubstituted Dithiocarbamic Acids

BY NORMAN K. SUNDHOLM AND ALLEN E. SMITH

A study of the reaction of 2,3-dichloro-1,4-naphthoquinone with salts of dithiocarbamic acids was undertaken in order to prepare new fungicides. With amine salts of methyl- and ethyldithiocarbamic acids the metathetical products IIa and IIb cyclize during heating by elimination of hydrogen chloride to produce compounds for which the structure 2-alkyliminonaphtho[2,3]-1,3-dithiole-4,9-dione (IIIa and IIIb) is in accord with the present experimental evidence. With dimethylammonium dimethyldithiocarbamate a quaternary salt is obtained. Since it gives the same hydrolysis product, believed to be naphtho[2,3]-1,3-dithiole-2,4,9-trione (VII), as 2-methyliminonaphtho[2,3]-1,3-dithiole-4,9-dione affords, and gives the latter on pyrolysis, it should also have the naphtho[2,3]-1,3-dithiole ring system. This is the first time that compounds having this ring system are reported. With ammonium dithiocarbamate the only product isolated was dibenzo[b,i]thianthrene-5,7,12,14-tetrone; a likely route for its formation is presented.

With the hope of preparing compounds which would combine the high fungitoxic activities of 2,3-dichloro-1,4-naphthoquinone¹ and of salts of certain dithiocarbamic acids,² a study of the reaction of the dichloroquinone with equimolar amounts of amine salts of alkyl-substituted dithiocarbamic acids and ammonium dithiocarbamate was made.

When amine salts of alkyl-substituted acids are employed, compounds which are believed to be derivatives of naphtho[2,3]-1,3-dithiole (I) are formed. This is the first time that compounds having this ring system are reported.

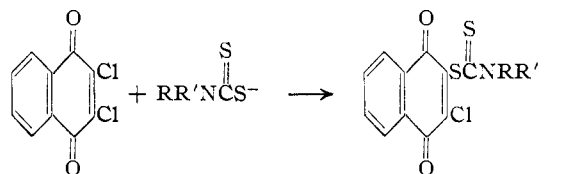


Treatment of 2,3-dichloro-1,4-naphthoquinone in aqueous suspension with an equimolar amount of methylammonium methyldithiocarbamate gives a crude product containing 9.12% chlorine. Very likely this product consists principally of IIa. When it is recrystallized from ethanol, a compound containing no chlorine and having an analysis consistent with IIIa or IV is obtained.

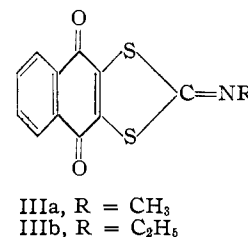
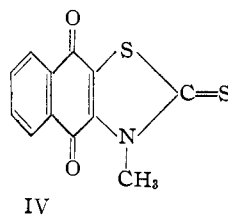
It has been well demonstrated that compounds containing the $\begin{matrix} S \\ || \\ -CNH- \\ | \\ SR \end{matrix}$ group are alkylated on the sulfur atom, $-C=N-$ being formed. This has

(1) W. P. ter Horst and E. L. Felix, *Ind. Eng. Chem.*, **35**, 1255 (1943).

(2) M. C. Goldsworthy, E. L. Green and M. A. Smith, *J. Agr. Research*, **66**, 277 (1943).



IIa, R = CH₃, R' = H
 IIb, R = C₂H₅, R' = H
 IIc, R = R' = CH₃



been observed with thioureas,³ thioamides,⁴ and, which concerns us more here, dithiocarbamic esters.⁵

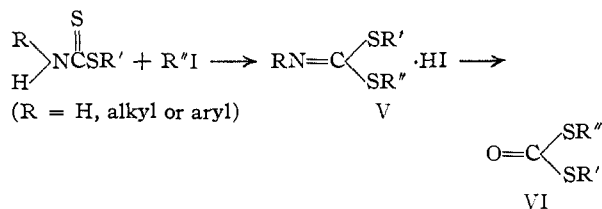
By treating dithiocarbamic esters having at least one hydrogen atom attached to nitrogen with an alkyl iodide Delépine obtained the hydriodide (V) of an imidodithiocarbamic ester. Acid hydrolysis of the imido ester gave the ester (VI).

Compound IIa is such a dithiocarbamic ester; in addition it contains an alkylating center, the 3-carbon atom linked to a reactive chlorine atom. If

(3) R. Connor, "Organic Sulfur Compounds," Chapt. 10 in H. Gilman's "Organic Chemistry," Sec. Ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 841.

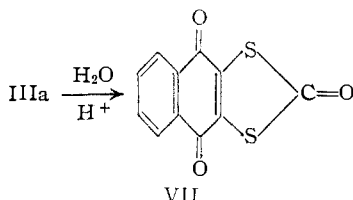
(4) S. Gabriel and Ph. Heymann, *Ber.*, **24**, 783 (1891).

(5) M. Delépine, *Bull. soc. chim. France*, [3] **27**, 57, 585 (1902); [3] **29**, 53, 59 (1903).

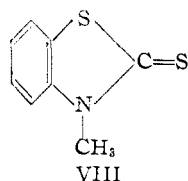


the thiono atom is alkylated, as would be expected by analogy with the cases cited above, compound IIIa, 2-methyliminonaphtho[2,3]-1,3-dithiole-4,9-dione, would be produced.

More evidence that the compound has the 1,3-dithiole structure is that acid hydrolysis readily affords a compound having the composition of naphtho[2,3]-1,3-dithiole-2,4,9-trione (VII). This hydrolysis appears to be a simple case of the hydrolysis of an imido ester to the ester and is analogous to that observed by Delépine (V → VI).



Morton and Stubbs⁶ determined the ultraviolet absorption spectrum of 3-methyl-2(3H)-benzothiazolethione (VIII) and found it to have absorption



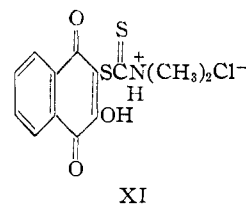
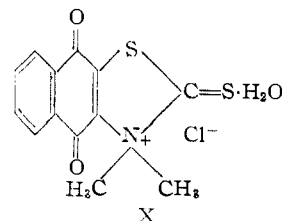
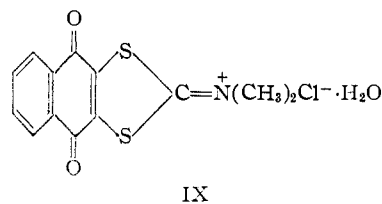
maxima at 324.5, 241 and 231 $m\mu$. The ultraviolet absorption spectrum of IIIa has been determined⁷ (Fig. 1); it has an absorption maximum at 266 $m\mu$ but none in the region of 325 $m\mu$.

Ethylammonium ethyldithiocarbamate gives with dichloronaphthoquinone a crude product containing 9.05% chlorine; when it is recrystallized from ethanol, a compound presumed to be IIIb is obtained.

The reaction of dichloronaphthoquinone with dimethylammonium dimethyldithiocarbamate in aqueous ethanol produces before heating a dark brown, thick mixture. On heating to reflux, the product is transformed to brown crystals which can be crystallized from water or dilute hydrochloric acid to give golden-yellow plates. The product is clearly a salt; it is water-soluble but benzene-insoluble, it can be precipitated from aqueous solution by the addition of hydrochloric acid or aqueous sodium chloride, and an aqueous solution gives with silver nitrate an immediate precipitation of silver chloride. The observed analytical values are in accord with the isomeric structures

(6) R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1321 (1939).

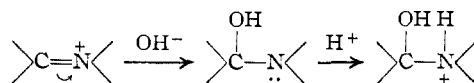
(7) The spectroscopic work was kindly performed by Messrs. R. R. Hampton and J. E. Newell of the General Laboratories of the United States Rubber Company.



Inasmuch as the dithiocarbamic ester, $(\text{CH}_3)_2\text{NCSSCH}_3$, does not form a hydrochloride either in dilute hydrochloric acid or in ether into which dry hydrogen chloride is bubbled, structure XI can be removed from consideration.

The quaternary salt is readily hydrolyzed by hot dilute acid to VII; at 215–225° and 0.5 mm. pressure it is pyrolyzed to IIIa. These two reactions show, barring parallel rearrangement of the nucleus in both instances, that the salt has the naphtho[2,3]-1,3-dithiole ring system. This would favor structure IX for the salt.

It has not been possible to obtain the salt in the anhydrous form; heating at 110° and 27 mm. pressure was without effect. It is possible that the water is bound at the $\text{C}=\text{N}^+$ double bond, the hydroxyl ion being linked to the electrophilic carbon atom and the proton to the then neutral nitrogen atom



The fact that an aqueous solution of the salt is acidic is consistent with this structure.

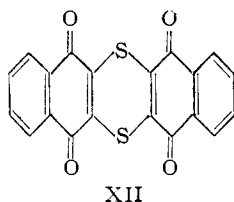
While the mechanism for the formation of the quaternary salt is not clear, it is likely that the product obtained on mixing the dichloronaphthoquinone with the dimethyldithiocarbamate salt has structure IIC. Although a thiol group cannot be formed by tautomeric shift, it could be formed by hydration of the thiocarbonyl group. Ring closure to IX by alkylation of the thiol group could then occur in the manner proposed for the formation of IIIa.

The ultraviolet absorption spectrum of the quaternary salt has been determined⁷ (Fig. 1).

When the salt is treated with aqueous sodium hydroxide, dibenzo[b,i]thianthrene-5,7,12,14-tetrone (XII) is formed. This compound has been previously prepared by Brass and Köhler⁸ by the treat-

(8) K. Brass and L. Köhler, *Ber.*, **55**, 2543 (1922).

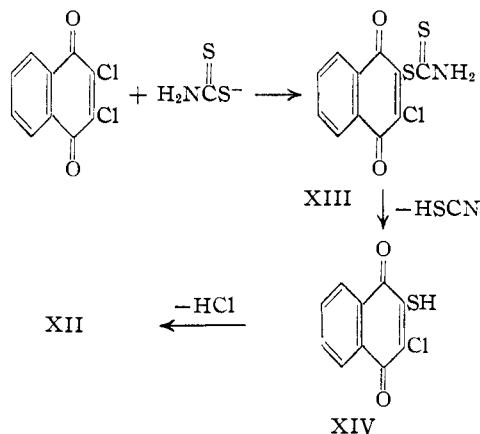
ment of 2,3-dichloro-1,4-naphthoquinone with sodium sulfide followed by oxidation.



The salt has been prepared by two other methods: by heating an intimate equimolar mixture of dichloronaphthoquinone with tetramethylthiuram disulfide to its fusion point (*ca.* 140°) and by chlorinating the product obtained from heating 1,4-naphthoquinone with tetramethylthiuram disulfide in solvent naphtha.

Treatment of 2,3-dichloro-1,4-naphthoquinone in aqueous suspension with an equimolar amount of ammonium dithiocarbamate affords a crude product which contains chlorine and sulfur, but only an insignificant amount of nitrogen. The mother liquor gives the qualitative test for thiocyanate ion with ferric ion. Crystallization of the crude product from chlorobenzene gives XII.

It is likely that the reaction proceeds as



It has been shown by von Braun⁹ that dithiocarbamic esters, H_2NCSSR , decompose readily under moderate heat to thiocyanic acid and the mercaptan, RSH . Compound XIII in the above equation is such an ester. The spontaneous loss of thiocyanic acid from it would give the mercaptoquinone XIV. This compound was not isolated, so it is not known whether it was actually present. It may be that as soon as a molecule of XIV is formed it condenses with another molecule to produce XII. This would account for the low chlorine content of the crude reaction product, 50% of that calculated for XIV, the chlorine being accounted for by secondary products and possible unreacted dichloronaphthoquinone.

Compounds IIIa, VII and the quaternary salt have been found to be only weakly fungicidal. They are approximately one-twentieth as effective as 2,3-dichloro-1,4-naphthoquinone in preventing infection of tomato foliage by the early blight fungus *Alternaria solani* in greenhouse tests.

(9) J. von Braun, *Ber.*, **35**, 3363 (1902).

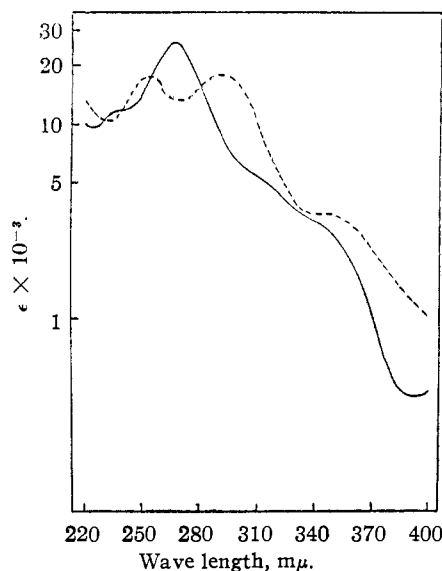


Fig. 1.—Absorption spectra in absolute ethanol: —, 2-methyliminonaphtho[2,3]-1,3-dithiole-4,9-dione (IIIa); - - - - -, quaternary salt.

Experimental¹⁰

2-Methyliminonaphtho[2,3]-1,3-dithiole-4,9-dione (IIIa).—A solution of methylammonium methylthiocarbamate prepared in the usual manner from 254 g. (0.84 mole) of 10.2% aqueous methylamine and 33.4 g. (0.44 mole) of carbon disulfide was added during 50 minutes to a well-agitated suspension of 90.8 g. (0.40 mole) of finely-ground 2,3-dichloro-1,4-naphthoquinone in 300 ml. of water containing a small amount of Nekal BX, a commercial wetting agent. After one-fifth of the dithiocarbamate solution had been added, the suspension had lost its finely-divided character, consisting, instead, of a soft sticky mass suspended in the aqueous layer. After stirring for 20 hours, the organic layer had again become solid and appeared to be quite finely divided. The mixture was filtered and the residue washed with water and air-dried to give 106 g. of maroon product melting and decomposing above 220°. Analysis showed this material to contain 9.12% chlorine, 3.69% nitrogen and 20.31% sulfur.

Fourteen grams of the crude product was added to 2 l. of ethanol and the mixture boiled for several minutes. It was filtered hot (3.5 g. of the product did not dissolve) and the filtrate allowed to stand in an ice-box for two days. The crystals which separated were recrystallized from ethanol to give 3.5 g. of red-violet crystals melting at 185–186°.

Anal. Calcd. for $C_{12}H_7NO_2S_2$: C, 55.17; H, 2.68; N, 5.36; S, 24.52. Found: C, 55.49; H, 3.14; N, 5.47; S, 24.32.

Acid Hydrolysis of 2-Methyliminonaphtho[2,3]-1,3-dithiole-4,9-dione (IIIa) to Naphtho[2,3]-1,3-dithiole-2,4,9-trione (VII).—Two-tenths gram of IIIa was added to a mixture of 10 ml. of concentrated hydrochloric acid, 50 ml. of water and 60 ml. of ethanol. The mixture was refluxed next for 45 minutes, the solid dissolving within 15 minutes. On cooling the mixture, tan crystals separated. They were crystallized twice from ethanol, treating the solution with Darco and cooling the filtrate quickly in an ice-bath each time, to give 0.04 g. (21%) of golden-yellow needles melting at 169–169.5°. When the hot solution is allowed to cool slowly to room temperature, the compound begins to crystallize in the form of the needles; however, after about an hour brown-red granules also begin to separate. After two days standing in contact with the mother liquor, the needles are transformed to the granules, which also melt at 169–169.5°. Since a mixed melting point is not depressed and the two forms give equivalent analytical values, it is apparent that they are merely crystalline modifications of the trione.

(10) The melting points are uncorrected.

Anal. Calcd. for $C_{11}H_8O_2S_2$: C, 53.23; H, 1.61; S, 25.81. Found: (for needles) C, 53.17; H, 1.50; S, 25.64; (for granules) C, 53.19; H, 1.51.

2-Ethyliminonaphtho[2,3]-1,3-dithiole-4,9-dione (IIIb).—Ethylammonium ethyldithiocarbamate was treated with 2,3-dichloro-1,4-naphthoquinone employing the procedure described for the preparation of the 2-methylimino compound. The crude product (before crystallization) was plum-colored, melted with decomposition at 231–235°, and contained 9.05% chlorine, 4.54% nitrogen and 22.19% sulfur. Some of this material was crystallized three times from ethanol to give small, dark red needles melting at 192–193°.

Anal. Calcd. for $C_{13}H_9NO_2S_2$: C, 56.73; H, 3.27; N, 5.09; S, 23.27. Found: C, 56.31; H, 3.16; N, 5.02; S, 23.28.

Preparation of the Quaternary Salt (a) from 2,3-Dichloro-1,4-naphthoquinone and Dimethylammonium Dimethyldithiocarbamate.—To a stirred mixture of 142 g. (0.82 mole) of 26% aqueous dimethylamine and 400 ml. of ethanol at 15° was added 32 g. (0.42 mole) of carbon disulfide in one portion. The temperature of the mixture rose to 35°. After cooling to about 25°, the mixture was stirred for one hour. This solution of dimethylammonium dimethyldithiocarbamate was added slowly to a well-agitated suspension of 90.8 g. (0.40 mole) of finely-ground 2,3-dichloro-1,4-naphthoquinone in 300 ml. of ethanol. During the addition, which took 25 minutes, the temperature of the reaction mixture rose from 24° to 50°. During the last stages of the addition, the dark brown reaction mixture became thick. It was heated and allowed to reflux for 20 minutes, after which the brown crystalline product was collected by filtration, washed with 150 ml. of hot ethanol and dried at 75°. The material was purified by dissolving it in 0.5 *N* hydrochloric acid at 85° at the rate of 1 g. per 100 ml., filtering the solution hot (which removed some brown insoluble by-product), and allowing the filtrate to cool in an ice-bath. The golden-yellow plates which crystallized were collected by filtration and dried at 70°; yield 86 g. (65%). The compound melts with decomposition at a point which varies with the rate of heating. When the capillary is immersed in the bath at 220° and the temperature of the bath raised 3–4° per minute, the compound melts with decomposition at 226–228°. The analytical sample was dried at 80° and about 50 mm. pressure.

Anal. Calcd. for $C_{13}H_9ClNO_2S_2 \cdot H_2O$: C, 47.34; H, 3.64; Cl, 10.77; N, 4.25; S, 19.42. Found: C, 47.42; H, 3.65; Cl, 11.06; N, 4.31; S, 19.58.

A sample which had been dried at 110° and 27 mm. pressure for 19 hours gave the same melting point and equivalent analytical results.

The compound turns to green-brown when exposed to light. It has a water solubility of 0.5% at 27°. A saturated solution has a pH of 5.3 at 29°. The compound dissolves in concentrated sulfuric acid with the evolution of hydrogen chloride. It is insoluble in hot benzene.

The compound is precipitated from a saturated aqueous solution by addition of aqueous sodium chloride or hydrochloric acid. Addition of aqueous silver nitrate gives an immediate precipitation of a nitric acid-insoluble material (silver chloride).

(b) From 2,3-Dichloro-1,4-naphthoquinone and Tetramethylthiuram Disulfide.—An intimate mixture of 5.7 g. (0.025 mole) of 2,3-dichloro-1,4-naphthoquinone and 6.0 g. (0.025 mole) of tetramethylthiuram disulfide was spread out in a thin layer on the bottom of a 1-l. beaker. The beaker was set on a hot-plate until the mixture melted (at about 140°) and almost immediately solidified to a brown solid. The product was crystallized three times from 0.5 *N* hydrochloric acid heated to 80°, treating with Darco each time, to give 2.9 g. (35%) of golden-yellow plates having the same melting point as the material prepared according to (a). A mixed melting point showed no depression.

(c) From 1,4-Naphthoquinone and Tetramethylthiuram Disulfide Followed by Chlorination.—A stirred suspension of 6.3 g. (0.04 mole) of 1,4-naphthoquinone and 4.8 g. (0.02 mole) of tetramethylthiuram disulfide in 100 ml. of solvent naphtha was heated. When the temperature reached 75°, solution was complete. When it reached 107–108°, the solution was suddenly transformed into a brown unstirrable mush. The mixture was filtered and the solvent naphtha pressed out of the filter cake as well as possible. The solid

product, which still smelled strongly of solvent naphtha after air-drying overnight, was added to 150 ml. of acetone and the mixture stirred for one hour. It was filtered and the residue washed with acetone and dried at 50° to give 8.1 g. of brown-gray product melting at 195–200° with decomposition. Attempts to purify this crude material by crystallization failed due to its insolubility. Analysis showed it to contain 4.00% nitrogen and 20.03% sulfur.

Three grams of this material was ground and suspended with stirring in 200 ml. of glacial acetic acid. While chlorine was passed into the suspension for 40 minutes at room temperature, the color changed from brown to orange-yellow. The mixture was filtered after stirring for one hour and the residue washed with 100 ml. of water (the washings were yellow) and dried to give 1.5 g. of yellow solid. It was crystallized once from 0.5 *N* hydrochloric acid (filtered hot to remove some insoluble material) to give 1.0 g. (30%) of golden-yellow plates having the same melting point as the material prepared according to (a). A mixed melting point showed no depression.

Hydrolysis of the Quaternary Salt (a) Acid Hydrolysis to Naphtho[2,3]-1,3-dithiole-2,4,9-trione (VII).—Six grams of the salt was added to 375 ml. of 0.5 *N* hydrochloric acid and the mixture refluxed for three hours. During the heating crystalline material separated. The reaction mixture was filtered hot. The residue was washed with warm water and dried to give 3.6 g. of brown-yellow crystals melting at 167–169°. By refluxing the mother liquor of the reaction mixture for an additional three hours, 0.5 g. more of crude product melting at 165–168° was obtained. The total yield of crude product was 4.1 g. (91%). Recrystallization from ethanol with quick cooling gave golden-yellow needles melting at 169–169.5°; a mixed melting point with the trione described above showed no depression.

(b) Alkaline Hydrolysis to Dibenzob[*b*,*i*]thianthrene-5,7,12,14-tetrone (XII).—To a stirred solution of 3.0 g. (0.009 mole) of the salt in 700 ml. of water at 40° was added dropwise 1.7 ml. of 6 *N* sodium hydroxide (0.010 mole). After standing for 15 minutes the brown suspension was filtered and the residue washed with water and dried. The crude green-brown product weighed 1.6 g. and melted at 280–290°. Some of this material was recrystallized from nitrobenzene. The nitrobenzene was removed from the deep purple crystals by washing with hot benzene. The melting point of XII, 302° (dec.), varies with the heating rate: it is the same as reported by Brass and Köhler.⁵

Anal. Calcd. for $C_{20}H_8O_4S_2$: C, 63.83; H, 2.13; S, 17.02. Found: C, 63.86; H, 2.01; S, 17.58.

Pyrolysis of the Quaternary Salt to 2-Methylimino-naphtho[2,3]-1,3-dithiole-4,9-dione (IIIa).—Two grams of the salt was placed in a vacuum sublimation apparatus evacuated to 0.5 mm. pressure and heated in a Woods metal-bath at 215–225°. Purple crystals mixed with a small amount of yellow solid collected on the cold finger. The product, which was scraped from the cold finger every three hours during 21 hours of heating, was crystallized twice from acetone to give 0.87 g. (55%) of deep purple needles melting at 185–186°. A mixed melting point with IIIa as prepared above showed no depression.

Reaction of 2,3-Dichloro-1,4-naphthoquinone with Ammonium Dithiocarbamate.—A solution of 35.2 g. (0.32 mole) of ammonium dithiocarbamate in a small amount of water was added during one-half hour to a well-stirred suspension of 68.1 g. (0.30 mole) of finely-ground 2,3-dichloro-1,4-naphthoquinone in 300 ml. of water containing a small amount of Nekal BX. The temperature of the mixture rose from 29° to 42° during the addition. The odor of hydrogen sulfide was evident during the mixing and for some time afterward. After the red-brown mixture had been stirred for 22 hours at room temperature, it was filtered. The filtrate gave, on addition of ferric chloride, the red color characteristic for the thiocyanate ion. The residue was washed with water until the washings were colorless. After drying, the fine red-brown solid weighed 45 g. and melted with decomposition at 270–280°. Analysis showed this material to contain 7.83% chlorine, 0.19% nitrogen and 14.64% sulfur. A small amount of this product was added to chlorobenzene and the mixture boiled for several minutes. It was filtered hot to remove some insoluble material. The dark brown crystals which separated on cooling were crystallized again from chlorobenzene to give deep purple needles melting at 302° with decomposition. A mixed melting point with dibenzob[*b*,*i*]thianthrene-5,7,12,14-

tetrone (XII) as prepared above was not depressed.

Acknowledgments.—The authors wish to express their appreciation to Drs. Frank R.

Mayo and Cheves Walling for their interest and suggestions.

NAUGATUCK, CONN.

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[CONTRIBUTION FROM THE WORCESTER FOUNDATION FOR EXPERIMENTAL BIOLOGY]

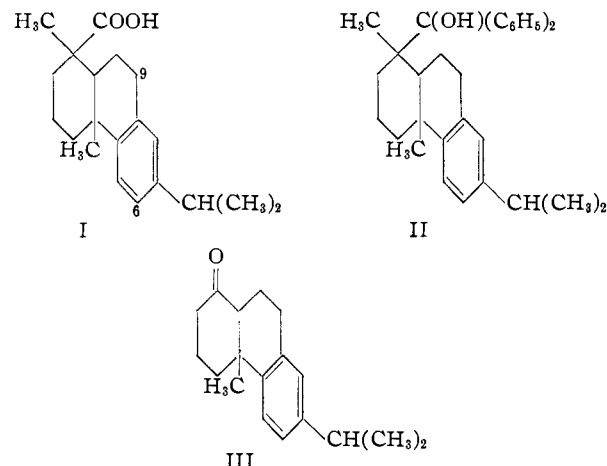
The Preparation and Properties of Dehydroabietophenone (*nor*-Dehydroabietyl Phenyl Ketone) and 6-Hydroxydehydroabietophenone¹

BY ROBERT P. JACOBSEN

The preparation and properties of dehydroabietophenone and its 6-hydroxy derivative are described. The facile oxidation of the methylene group at C₉ in dehydroabietic acid and its derivatives is confirmed.

In view of reports^{2,3} of the possible estrogenic activity of certain resin acid derivatives, it seemed of interest to prepare for pharmacological examination compounds related to dehydroabietic acid (I) in which the carboxyl and one or more of the alkyl groups were replaced by oxygen functions.

In this connection Zeiss⁴ has reported the oxidation of non-crystalline material considered to be diphenyldehydroabietinol (II) with chromic acid at 80–90° forming benzophenone and a non-crystalline neutral product to which the structure III was assigned. Recently Brossi, Gutmann



and Jeger⁵ have prepared pure II, m.p. 139.5–140°, and have demonstrated that the compound undergoes decomposition, both during attempted distillation at 11 mm. and on heating 30 minutes at about 220° in vacuum, with the production of a mixture of C₁₉H_{26–28} hydrocarbons together with benzophenone and benzhydrol. The principal hydrocarbon, IV, obtained in the pyrolysis of II was oxidized at 80° with chromic acid forming not III but a mixture of the 9-oxo derivatives, V and VI. These observations have been confirmed by Zeiss⁶ so that the possible susceptibility of II to chromic acid degradation is still in question.

(1) The work described in this paper was supported by a grant from G. D. Searle & Company.

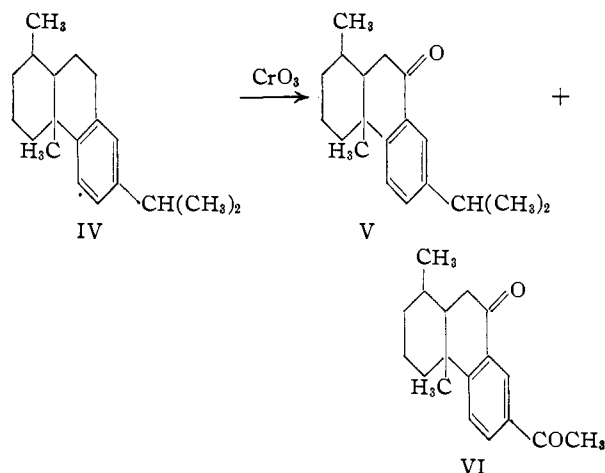
(2) L. F. Fieser and W. P. Campbell, *THIS JOURNAL*, **61**, 2530 (1939); M. M. Baizer, M. Karnowsky and W. G. Bywater, *ibid.*, **72**, 3800 (1950).

(3) C. W. Brandt and D. J. Ross, *Nature*, **161**, 892 (1948).

(4) H. H. Zeiss, *THIS JOURNAL*, **70**, 858 (1948); **69**, 302 (1947).

(5) A. Brossi, H. Gutmann and O. Jeger, *Helv. Chim. Acta*, **33**, 1730 (1950).

(6) H. H. Zeiss, *THIS JOURNAL*, **73**, 497 (1951).



Brossi, Gutmann and Jeger succeeded in preparing III by the ozonolysis of the hydrocarbon mixture formed in the phosphorus pentachloride⁷ dehydration-rearrangement of dehydroabietinol, a reaction sequence which achieves one of the aims mentioned above.

This report describes the properties of dehydroabietophenone (IX) prepared for a similar type of degradation. In the characterization of the resinous phenyl ketone several derivatives analogous to 9-oxodehydroabietic acid⁸ and V were obtained by chromic acid oxidation at 20–35°.

In the preparation of IX from dehydroabietyl chloride (VII) and diphenylcadmium the product was obtained in the form of a viscous resin soluble in pentane and showing no tendency to crystallize on fractional elution with pentane from a column of alumina. This product, on prolonged heating at 130° in methanolic hydroxylamine solution, formed an amorphous solid with only three-fifths the nitrogen content calculated for the oxime; attempts to prepare a dinitrophenylhydrazone were also unsuccessful.

The reduction of crude dehydroabietophenone with aluminum isopropoxide afforded a semi-crystalline product from which crystalline phenyldehydroabietinol (XI) was isolated (about 40% yield based on the acid) by virtue of its slight solubility in pentane. The pentane-soluble fraction was heated with dinitrobenzoyl chloride in pyridine providing 7% (based on the acid) of the dinitro-

(7) L. Ruzicka and J. Meyer, *Helv. Chim. Acta*, **5**, 589 (1922).

(8) A. E. Drake, U. S. Patent 2,434,643.