ether layer was separated and the aqueous layer extracted with 6 portions of 25 ml. of ether. Removal of the solvent after drying gave a residue which was distilled to give a yellow liquid, b.p. 102–105° (4.5 mm.), 3.5 g. (20%). A large tarry residue was left in the distilling flask. Redistillation gave 3.0 g. (17%), $n^{25}\text{D}$ 1.5122, $d^{25}{}_4$ 0.9646, of 2-N-dimethylamino-4-butylpyrimidine. On standing in a closed flask for 24 hours this compound turns red.

Anal. Calcd. for $C_{10}H_{17}N_3$: C, 67.00; H, 9.55; N, 23.4. Found: C, 66.71; H, 9.65; N, 23.2.

The picrate was prepared in the usual manner, m.p. 80–81° and was recrystallized from ethanol, m.p. 80.5–81.5°.

Anal. Calcd. for $C_{16}H_{20}N_6O_7$: N, 20.8. Found: N, 21.2.

The reaction was repeated using 0.9 mole of *n*-butyllithium and 36.9 g. (0.3 mole) of 2-N-dimethylaminopyrimidine. The reaction mixture was treated in the same fashion as described in the previous experiment. There was obtained a yellow liquid which turned red after 24 hours, b.p. 124–135° (2.5 mm.), 12 g. (17%). Redistillation of the liquid gave a yellow distillate, b.p. 140–145° (4.5 mm.), 9 g. (13%), $n^{25}\text{D}$ 1.5030, which is probably the dibutyl derivative, 2-N-dimethylamino-4,6-di-*n*-butylpyrimidine.

Anal. Calcd. for $C_{14}H_{25}N_3$: C, 71.43; H, 10.70; N, 17.8. Found: C, 71.69; H, 10.54; N, 17.6.

These compounds fluoresce a blue color under ultraviolet light.

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer. An aqueous buffered solution, *p*H 7.0 ± 0.02, was used as the solvent in order to compare the curves with those reported by reference 3.

Acknowledgment.—We are grateful to Dr. Chester Stock and his group at the Sloan–Kettering Institute for testing these compounds for their effectiveness against sarcoma 180. We are also grateful to the National Health Institute for support.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

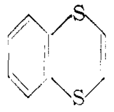
Heterocyclic Vinyl Ethers. IV. Benzo-1,4-oxathiadiene and Benzo-1,4-dithiadiene[1,2]

BY WILLIAM E. PARHAM AND JOHN D. JONES

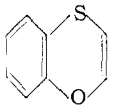
RECEIVED OCTOBER 2, 1953

The synthesis (three methods) and proof of structure of benzo-1,4-oxathiadiene (II) are described and the polymerization, ethanolysis, bromination, hydrolysis and electrophilic substitution of this ring system are compared to analogous reactions with benzo-1,4-dithiadiene (I). This paper describes a new synthesis and certain new reactions of I, and includes a study of osazone formation from β-oxy- and β-thiohydrazones.

A recent study[3] of the chemistry of benzo-1,4-dithiadiene (I) has shown that the sulfur-containing ring of this system exhibits the stability, and some of the reactions (*i.e.*, electrophilic substitution), usually associated with molecules possessing a considerable degree of resonance stabilization.



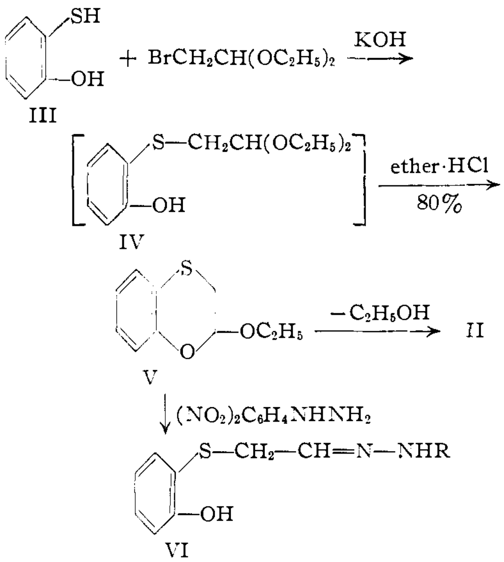
I



II

This report describes a study of the synthesis and reactions of an analogous system, benzo-1,4-oxathiadiene (II). Interest in this new heterocyclic system was twofold: (1) to compare the properties and stability of systems I and II, and (2) to accumulate data which will be of ultimate value in regard to a final clarification of the relative electronic effects of oxygen and sulfur.[4]

A study of the reaction sequence outlined in the following equations was chosen initially as a route to benzo-1,4-oxathiadiene for:



(1) the method had proved highly successful for the preparation of I,[3] and (2) use of this method would allow a direct comparison to be made concerning the relative ease of formation of the double bond in the heterocyclic rings of I and II.

2-Ethoxybenzo-1,4-oxathiene (V) was obtained in 80% over-all yield from the reaction of equimolar quantities of monothiocatechol (III), diethyl bromoacetal and potassium hydroxide in absolute ethanol solution. The intermediate phenolic acetal IV was not isolated, but instead was treated with

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[1] This work was supported by the Office of Ordnance Research, Contract Number DA-11-022-ORD-571.

[2] From the Ph.D. Thesis of John D. Jones, University of Minnesota (1953).

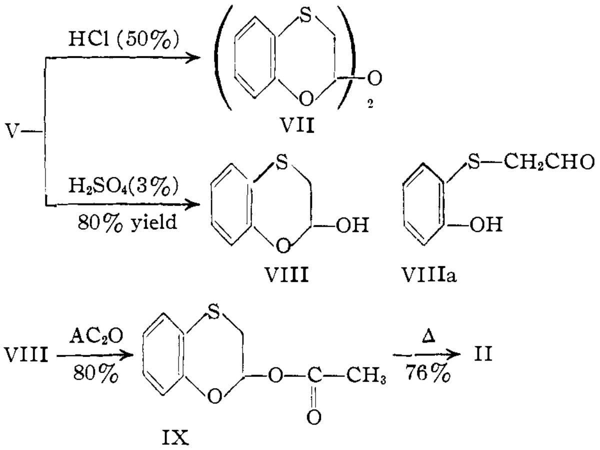
[3] W. E. Parham, T. M. Roder and W. R. Hasek, THIS JOURNAL, **75**, 1647 (1953).

[4] *A priori* it seemed reasonable to assume that the type of resonance responsible for the greater stability of thiophene relative to furan (*i.e.*, valence shell expansion of sulfur) would make a greater contribution to the structure of I (two sulfur atoms) than to the structure of II (one sulfur atom); hence the dithia compound should be more stable than the oxathia compound. On the other hand, oxygen can release electrons in the direction of its covalent bonds more readily than sulfur, and a combination of resonance involving release of electrons from oxygen and sulfur and expansion of the valence shell of sulfur should impart a noticeable degree of stabilization to the 1,4-oxathiadiene system. *Cf.* W. E. Parham, J. Gordon and J. Swalen, *ibid.*, **74**, 1824 (1952).

ethereal hydrogen chloride to effect the intramolecular acetal interchange. The acetal V was further characterized by: (1) its conversion into 2-hydroxyphenylthioacetaldehyde 2,4-dinitrophenylhydrazone (VI) by reaction with 2,4-dinitrophenylhydrazine, (2) its conversion, in 79% yield, to 2-butoxybenzo-1,4-oxathiene by reaction with excess *n*-butyl alcohol containing hydrogen chloride, and (3) its conversion, in 82% yield, to the diethyl mercaptal of 2-hydroxyphenylthioacetaldehyde by reaction with excess ethyl mercaptan in acid.

The liquid phase dealkoxylation of V by action of catalytic amounts of phosphorus pentoxide at 180–190°, in an atmosphere of nitrogen, gave II in conversion yields of 0–20%, together with considerable quantities (34–74%) of unchanged starting material. The ease of dealkoxylation of V was in sharp contrast to the ease of dealkoxylation of 2-ethoxybenzo-1,4-dithiene,[3] for under identical conditions the dealkoxylation of 2-ethoxybenzo-1,4-dithiene gave a 72% yield of I. Further evidence for the relative stability of the acetal V and the dithia derivative, 2-ethoxybenzo-1,4-dithiene toward dealkoxylation, was obtained by studies of their vapor phase dealkoxylation over alumina in an inert atmosphere. V was recovered in 73% yield after contact with alumina at 270°. 2-Ethoxybenzo-1,4-dithiene, on the other hand, gave benzo-1,4-dithiadiene (I) in 58% yield by action of alumina at 250°, and I in 49% yield at 300°.

Attempts to effect the conversion of V into II by reaction with *p*-toluenesulfonic acid[4] or by reaction with aluminum *t*-butoxide[5] were unsuccessful. The most satisfactory synthesis developed for II proved to be the dehydration of 2-hydroxybenzo-1,4-oxathiene (VIII).

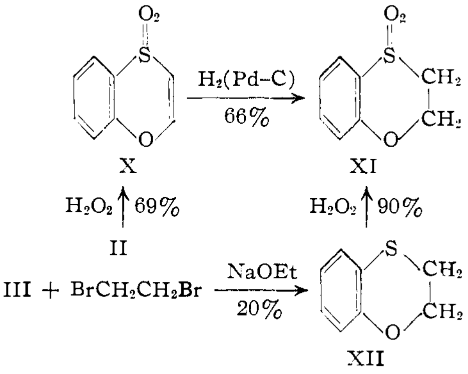


Initial attempts to hydrolyze V with hot 50% hydrochloric acid resulted in the formation of a crystalline solid, which proved to be bis-(2-benzo-1,4-oxathienyl) ether (VII). Evidence for the structure of VII was: (1) the infrared spectrum was consistent with this structure in that hydroxyl and carbonyl absorption were absent, (2) the observed composition (C and H) agreed with values calculated for VII, and (3) reaction of the product with 2,4-dinitrophenylhydrazine and hydrochloric acid gave VI. Prolonged action of hot 3% sulfuric acid upon the acetal V resulted in an 80% yield of the white crystalline aldehyde VIII. VIII readily gave VI by reaction with 2,4-dinitrophenylhydrazine. The infrared absorption spectrum of the aldehyde established its structure as VIII and not VIIIa, for no aldehyde C–H absorption (2770–2820 cm.^{-1}) or carbonyl absorption were present.

2-Acetoxybenzo-1,4-oxathiene (IX) was obtained in 80% yield by acetylation of VIII with acetic anhydride in pyridine. The acetate readily formed the same derivative VI as the parent aldehyde when treated with 2,4-dinitrophenylhydrazine. The infrared spectrum of the acetate established it to be a derivative of the cyclic structure VIII and not of the open chain isomer VIIIa (*i.e.*, no aldehyde C–H absorption, and a single ester carbonyl band at 1755 cm.^{-1}).

Benzo-1,4-oxathiadiene (II) was obtained in 76% yield by pyrolytic deacetoxylation of IX at 450–460° in an atmosphere of nitrogen. The fact that high yields of II were obtained by this process is evidence for the thermal stability of the olefinic function.[6]

Reactions which constitute proof of structure of benzo-1,4-oxathiadiene are summarized in the equations below. These reactions are self-explanatory and details are found in the experimental section of this report.



The results of a study of the properties and chemical reactivity of benzo-1,4-oxathiadiene are discussed in connection with results of a comparable investigation of benzo-1,4-dithadiene (I), made previously,[3] or as a part of this work.

Benzo-1,4-oxathiadiene, unlike benzo-1,4-dithiadiene (I), is sensitive to oxygen (air) at room temperature. Samples of II could be stored indefinitely in an atmosphere of nitrogen; however, when the olefin was exposed to air, it slowly changed to a gelatin-like material, which was composed primarily of a white solid polymer with the formula $(C_8H_6OS\cdot O)_n$. McElvain[7] observed a similar phenomenon during the autoxidation of certain cyclic ketene acetals, and the reaction of II with air can be formulated accordingly, as shown in the equation

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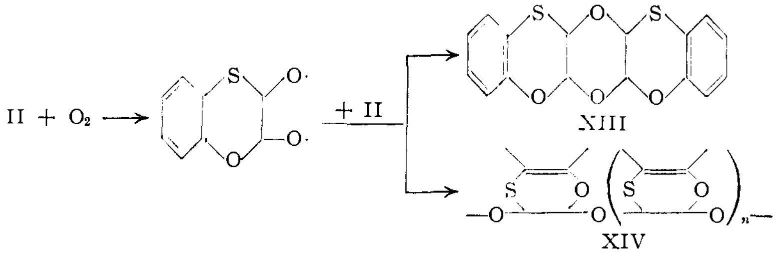
(5) S. M. McElvain and W. R. Davies, THIS JOURNAL, **73**, 1400 (1951).

(6) II also was obtained in 12% yield by the reaction of VIII with phosphorus pentoxide in pyridine. The low yield of II in this reaction can be attributed to the fact that as soon as the reaction begins the oxide is coated with products and is unavailable for further reaction.

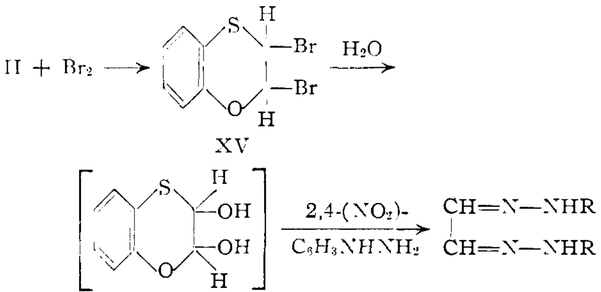
(7) S. M. McElvain and C. L. Aldridge, THIS JOURNAL, **75**, 3993 (1953).



Benzo-1,4-oxathiadiene reacted with polymerization catalysts in a manner typical of vinyl ethers. The olefin was polymerized slowly by reaction with benzoyl peroxide, and rapidly by reaction with boron trifluoride etherate.

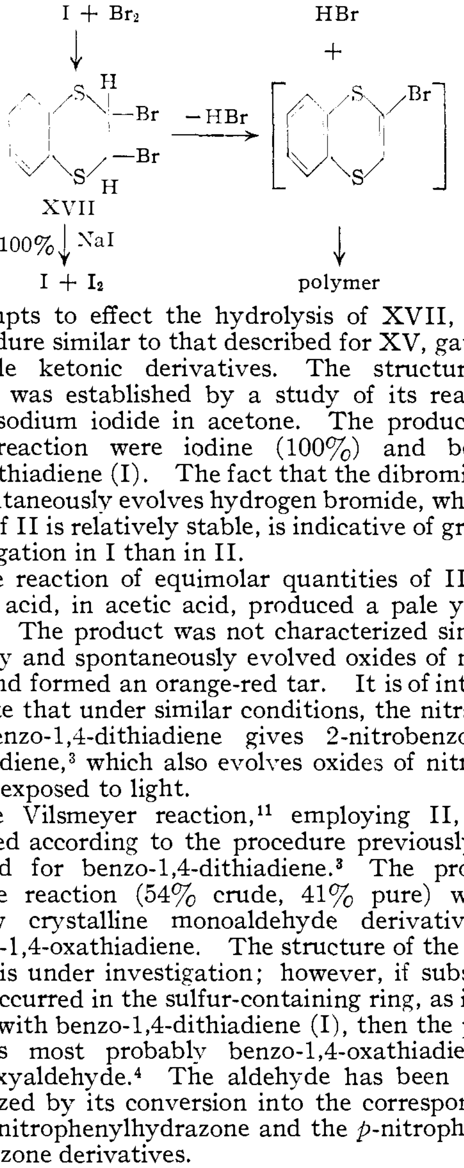
It was anticipated, by analogy to the facile acid-catalyzed addition of ethanol to *p*-oxathiene,[4] that the reaction of II with acidic ethanol would give 2-ethoxybenzo-1,4-oxathiene (V). The results of several experiments revealed that the Δ-2-double bond of II exhibits a stability atypical of vinyl ether structures. When a solution of II in ethanol (containing a trace of hydrogen chloride) was allowed to stand for 20 hours at room temperature, 78% recovery of II was obtained.[8] II was recovered in 62% yield (the remaining material was accounted for as polymer) after being heated for four hours at the reflux temperature in the presence of 0.36 *N* hydrogen chloride in ethanol. The ethanolysis of II was accomplished by heating a solution of II, ethanol and hydrogen chloride (*ca.* 0.47 *N*) under reflux for 85 hours. The reaction product contained 38% of unchanged II and 56% of V. The acetal V was identified by its boiling point, refractive index and its conversion, by reaction with 2,4-dinitrophenylhydrazine, into VI (81% yield). Benzo-1,4-dithiadiene (I) also has been reported to be quite resistant to ethanolysis.[9]

The reaction of equimolar quantities of II and bromine resulted in the formation of an 89% yield of 2,3-dibromobenzo-1,4-oxathiene (XV), m.p. 105–106°). The dibromide showed no obvious tendency to evolve hydrogen bromide, and appeared to be stable.



Hydrolysis of the dibromide was accomplished without difficulty (a reaction typical of α-haloethers) in aqueous ethanol, and the isolation of high yields of glyoxal as the 2,4-dinitrophenylosazone (55%), or the phenylosazone (58%), from the hydrolysate mixtures served to establish the structure of XV.

Equimolar quantities of I and bromine were allowed to react under conditions similar to those employed for the bromination of II and from this reaction there was obtained an 81% yield of 2,3-dibromobenzo-1,4-dithiene (XVII). This dibromide proved to be very unstable and rapidly evolved hydrogen bromide to give a purple alcohol-soluble solid,[10] which was presumably a polymeric sulfonium salt.



Attempts to effect the hydrolysis of XVII, by a procedure similar to that described for XV, gave no isolable ketonic derivatives. The structure of XVII was established by a study of its reaction with sodium iodide in acetone. The products of this reaction were iodine (100%) and benzo-1,4-dithiadiene (I). The fact that the dibromide of I spontaneously evolves hydrogen bromide, whereas that of II is relatively stable, is indicative of greater conjugation in I than in II.

The reaction of equimolar quantities of II and nitric acid, in acetic acid, produced a pale yellow solid. The product was not characterized since it rapidly and spontaneously evolved oxides of nitrogen and formed an orange-red tar. It is of interest to note that under similar conditions, the nitration of benzo-1,4-dithiadiene gives 2-nitrobenzo-1,4-dithiadiene,[3] which also evolves oxides of nitrogen when exposed to light.

The Vilsmeyer reaction,[11] employing II, was effected according to the procedure previously described for benzo-1,4-dithiadiene.[3] The product of the reaction (54% crude, 41% pure) was a yellow crystalline monoaldehyde derivative of benzo-1,4-oxathiadiene. The structure of the aldehyde is under investigation; however, if substitution occurred in the sulfur-containing ring, as is the case[3] with benzo-1,4-dithiadiene (I), then the product is most probably benzo-1,4-oxathiadiene-3-carboxyaldehyde.[4] The aldehyde has been characterized by its conversion into the corresponding 2,4-dinitrophenylhydrazone and the *p*-nitrophenylhydrazone derivatives.

The hydrolysis of benzo-1,4-oxathiadiene (II) in the presence of 2,4-dinitrophenylhydrazine was expected to result in the formation VI, for this derivative is known to form readily, at room temperature, when either VIII or V is treated with 2,4-

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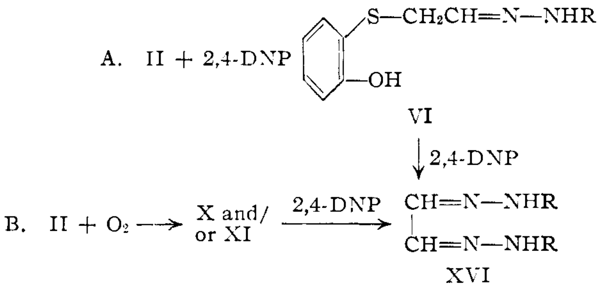
[8] When these reaction conditions are applied to *p*-oxathiene an 87% yield of addition product results. *Cf.* ref. 4.

[9] Under mild conditions benzo-1,4-dithiadiene is recovered essentially unchanged from similar reaction mixtures. When I is treated for four hours with boiling 2.5 *N* hydrogen chloride in ethanol, the product (87% recovery) is composed of 87% unchanged I and 13% 2-ethoxybenzo-1,4-dithiene. *Cf.* ref. 3.

[10] This material has not been obtained in a state of purity sufficient for characterization.

[11] The Vilsmeyer reaction with alicyclic bis-divinyl sulfides, vinyl sulfides and vinyl ethers will be reported in a subsequent report.

dinitrophenylhydrazine. Instead, glyoxal 2,4-dinitrophenylosazone was slowly formed at room temperature. Two paths, which are summarized in the following equations, were considered for this reaction.



The formation of osazones from β-thioaldehydes or β-thiohydrazones apparently had not been reported previously; however, Cass[12] had previously shown that the 2,4-dinitrophenylhydrazone of 2-hydroxyethyloxyacetaldehyde (XVIIIa) gave glyoxal 2,4-dinitrophenylosazone upon reaction with excess 2,4-dinitrophenylhydrazine. A study of the reaction of osazone formation from β-oxy- and β-thiohydrazones (XVIII and VI) was made in order to properly evaluate path A.

$$\text{R'-y-CH}_2\text{CH=N—NHR} \xrightarrow{\text{2,4-D, H}^+} \text{XVI}$$

$$\text{XVIIIa (R'} = \text{HOCH}_2\text{CH}_2\text{—, y} = \text{O)}$$

$$\text{XVIIIb (R'} = \text{HOCH}_2\text{CH}_2\text{—, y} = \text{S)}$$

$$\text{R} = \text{2,4-dinitrophenyl}$$

It was found that the β-oxyhydrazone (XVIIIa) was converted to the osazone XVI much more readily than the β-thiohydrazone (XVIIIb). For example, a 29% yield of XVI was obtained from XVIIIa and 2,4-dinitrophenylhydrazine (room temperature for five days), whereas only a 6% yield of XVI was obtained from a similar reaction employing XVIIIb. Similar results were obtained when XVIIIa or XVIIIb were heated for one hour in the presence of 2,4-dinitrophenylhydrazine and then allowed to stand at room temperature for two days; in these cases 73 and 54% yields XVI were obtained, respectively.[13] The fact that osazones do result from the reaction of β-thiohydrazones and 2,4-dinitrophenylhydrazine established path A as a possible route to the formation of XVI from II; however, this scheme was rendered untenable when it was found that the reaction of VI and 2,4-dinitrophenylhydrazine did not give XVI when the reaction was carried out at room temperature.[14]

It was shown that the formation of XVI from II did involve reaction with oxygen. A reaction mixture containing II, 95% ethanol containing hydrochloric acid and 2,4-dinitrophenylhydrazine, was divided into two portions, one of which was exposed to air and the other stored under nitrogen. The reaction mixture that was exposed to air precipitated glyoxal 2,4-dinitrophenylosazone, whereas the mixture stored under nitrogen gave only VI. These experiments furnish direct evidence to indicate that X and/or XI, derivatives of glyoxal, are probable intermediates in the reaction.

Experimental

2-Ethoxybenzo-1,4-oxathiene (V).—Diethyl bromoacetal (105 g., 0.533 mole) was added dropwise to a well-stirred solution prepared from monothioglycol[15] (67.2 g., 0.533 mole, b.p. 80–88° (9.0 mm.), $n^{19.5}\text{D}$ 1.6043) and potassium hydroxide (35.2 g. (85%), 0.533 mole) in absolute ethanol (250 ml.), and the resulting solution was heated at the reflux temperature for two hours. An atmosphere of nitrogen was maintained above the mixture during the entire reaction. Magnesium sulfate (5 g.) was added to the cooled reaction mixture to remove traces of water, and the insoluble salts were then removed and washed with small portions of absolute ethanol. Alcohol was then removed from the filtrate and the combined washings, and 15 ml. of ether, saturated with hydrogen chloride at 25°, was added to the cool (25°) residue. The resulting solution was allowed to stand at room temperature for 24 hours in a stoppered flask, and was then neutralized by the addition of anhydrous sodium carbonate. The mixture was then filtered and the filtrate distilled to give 84 g. of V (b.p. 129–136° (9.0 mm.), 80.4% yield, $n^{25}\text{D}$ 1.5713). The product was refractionated (b.p. 125 (4 mm.), $n^{20.5}\text{D}$ 1.5732) for analysis.

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.21; H, 6.17. Found: C, 61.49; H, 6.04.

2-Hydroxyphenylthioacetaldehyde 2,4-Dinitrophenylhydrazone (VI).—The procedure used was that normally employed for the preparation of 2,4-dinitrophenylhydrazones from aldehydes. VI was prepared readily from V, at room temperature, and was recrystallized from ethanol; golden-yellow plates, m.p. 132–133°.

Anal. Calcd. for $C_{14}H_{12}O_5SN_4$: C, 48.28; H, 3.47. Found: C, 48.48; H, 3.59.

2-Butoxybenzo-1,4-oxathiene.—A mixture of V (36.4 g., 0.186 mole), dry *n*-butyl alcohol (50 g., 0.68 mole) and hydrogen chloride in ether (8 drops, 7.5 *N* HCl), was heated at the reflux temperature for one hour. The solution was treated with anhydrous sodium carbonate (4 g.) to remove the acid, the solids were removed, and the resulting solution was fractionally distilled to give 32.9 g. (79%) of 2-butoxy-1,4-oxathiene (b.p. 95–96 (0.25 mm.), $n^{23}\text{D}$ 1.5498). The reaction of this acetal with 2,4-dinitrophenylhydrazine and acid gave VI (m.p. and mixed m.p. 132–133°).

Anal. Calcd. for $C_{12}H_{16}O_2S$: C, 64.27; H, 7.19. Found: C, 64.55; H, 7.42.

Diethyl 2-Hydroxyphenylthioacetaldehyde Mercaptal.—A mixture of V (10.5 g., 0.0536 mole), ethyl mercaptan (16.6 g., 0.268 mole), glacial acetic acid (20 ml.) and concentrated hydrochloric acid (25 ml.) was allowed to stand at room temperature for six days. The excess ethyl mercaptan was removed by evaporation, and the remaining material (two-phase) was extracted with four 50-ml. portions of ether. The aqueous solution was neutralized with sodium carbonate and extracted with ether. The combined ether extract was washed with water and dilute bicarbonate, and was then dried (magnesium sulfate) and distilled. The mercaptal (12.1 g., $n^{25}\text{D}$ 1.5943, 82% yield) was collected at 136–139° (0.1 mm.).

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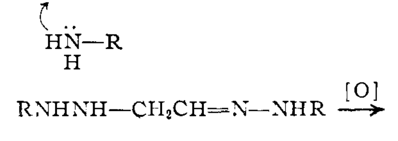
[12] W. E. Cass, THIS JOURNAL, **69**, 1500 (1947).

[13] In the reaction of XVIIIb with 2,4-DNP the odor of monothioglycol was evident; however, no attempt was made to isolate this product. The cleavage of these ethers and sulfides by reaction with 2,4-DNP bears a formal resemblance to the decomposition of β-bromoethers by reaction with metals (Mg, Zn, etc.).



[14] *E.g.*, the same reaction conditions employed with II. It is of interest to note, however, that the reaction of VI and 2,4-dinitrophenylhydrazone, at elevated temperatures (reflux temperature of ethanol for five days) did give an excellent yield (79%) of XVI.

[15] P. Friedlander and F. Mauthner, *Chem. Zentr.*, **75**, **II**, 1176 (1904).

Anal. Calcd. for $C_{12}H_{18}OS_3$: C, 52.55; H, 6.62. Found: C, 52.85; H, 6.83.

Bis-(2-benzo-1,4-oxathienyl) Ether (VII).—A mixture of V (5.5 g., 0.028 mole) and aqueous hydrochloric acid (20 ml., 6 *N*) was heated on a steam-bath, and nitrogen was passed through the mixture. After 1.5 hours most of the aqueous phase had evaporated. The oil was extracted with ether, and the ether was removed by distillation. The residual oil was treated with alcohol (50 ml.) and the tan solid that precipitated was collected and recrystallized from chloroform–petroleum ether. VII (1.4 g., 31% yield) was obtained as white needles melting at 119–120°.

Anal. Calcd. for $C_{16}H_{14}S_2O_3$: C, 60.38; H, 4.43. Found: C, 60.25; H, 4.58.

The reaction of VII with 2,4-dinitrophenylhydrazine, using the conditions normally employed for the conversion of an aldehyde to a 2,4-dinitrophenylhydrazone, proceeded rapidly (5 min.) at 95° to give VI (m.p. and mixed m.p. 131–132°).

2-Hydroxybenzo-1,4-oxathiene (VIII).—A mixture of V (57 g., 0.291 mole) and dilute sulfuric acid (200 ml., 3% sulfuric acid) was heated at the reflux temperature for 34 hours, and the resulting mixture was steam distilled until the distillate was clear (*ca.* 400 ml. of distillate containing 2 g. of water-insoluble oil). The residual solution from the steam distillation was made basic by the addition of excess sodium bicarbonate and was then extracted with ether (400 ml.). The combined ether extract was dried (magnesium sulfate) and the ether was removed. The residue was dissolved in benzene, and petroleum ether was added until the solution became cloudy. The light tan needles (37.5 g., 79.7%, m.p. 58–61°) were further purified by recrystallization from benzene–petroleum ether to give transparent white needles melting at 62–62.5°.

Anal. Calcd. for $C_8H_8O_2S$: C, 57.14; H, 4.80. Found: C, 57.18; H, 4.87.

VIII was readily soluble in 10% sodium hydroxide and gave a slow, positive test with Fuchsin aldehyde reagent. VI (m.p. and mixed m.p. 131–133°) was readily formed, at room temperature, when VIII was treated with 2,4-dinitrophenylhydrazine under conditions normally employed for the conversion of aldehydes to their 2,4-dinitrophenylhydrazones.

2-Acetoxybenzo-1,4-oxathiene (IX).—A mixture of VIII (25.0 g., 0.149 mole), acetic anhydride (100 ml.) and pyridine (100 ml.) was heated at the reflux temperature for 20 minutes, and was then reduced in volume to approximately 50 ml. by distillation at 27 mm. The remaining material was cooled and 200 ml. of water was added. When the excess acetic anhydride had been hydrolyzed, the mixture was neutralized with bicarbonate and extracted with ether. IX, obtained from the ether extract, was recrystallized from benzene–petroleum ether; tan needles, m.p. 49–55°, 25.1 g., 80.3% yield. Further purification of the acetate, by crystallization from benzene–petroleum ether, gave colorless, transparent needles melting at 55–55.5°.

Anal. Calcd. for $C_{10}H_{10}O_3S$: C, 57.14; H, 4.80. Found: C, 57.23; H, 5.04.

The reaction of IX with 2,4-dinitrophenylhydrazine in acid, at room temperature, gave VI (m.p. and mixed m.p. 131–133°).

Benzo-1,4-oxathiadiene (II). A. Dealkoxylation of V with P_2O_5.—In a distilling apparatus filled with an 8-cm. glass-helices packed column were placed 27.4 g. (0.14 mole) of 2-ethoxybenzo-1,4-oxathiene (V) and 0.1–0.2 g. of phosphorus pentoxide. A tube was inserted below the surface of the liquid and a slow stream of oxygen-free nitrogen was was passed through the liquid. Arrangement was also made to collect the alcohol formed during the reaction in a Dry Ice trap. The material was maintained at 180–185° for 5.25 hours. A total of 1.7 g. of alcohol (26.5%) was collected in the Dry Ice trap. The reaction mixture was then distilled at reduced pressure. The material boiling below 55° (0.07 mm.), 4.2 g., n^{23}D 1.6145–1.6091, was principally benzo-1,4-oxathiadiene (II). The material boiling above 55°, 12.9 g., n^{23}D 1.5748, was principally recovered starting material. Crude II was redistilled and a sample boiling at 49° (0.08 mm.), n^{25}D 1.6129, was analyzed.

Anal. Calcd. for C_8H_6OS: C, 63.97; H, 4.03. Found: C, 63.86; H, 4.27.

This reaction was repeated about twenty times and variable results were obtained (0–20% yield).

B. Dehydration of 2-Hydroxybenzo-1,4-oxathiene (VIII) with P_2O_5.—Phosphorus pentoxide (22.4 g., 0.149 mole) was added to a solution of VIII (25.0 g., 0.149 mole) in pyridine (35.5 g.). The mixture was warmed on a steam-bath to about 60°, and a vigorous reaction occurred. The mixture was cooled to room temperature, the large lumps that had formed were broken, and the supernatant pyridine was decanted into a distilling flask. The pyridine was removed by distillation, and 5.6 g. of material was collected at 50–100° (0.4 mm.). The solid (from which the pyridine was decanted) was agitated with benzene and the excess phosphorus pentoxide decomposed with water. The benzene extract was dried and the oil obtained when the benzene was removed, was combined with the product obtained from the distillation. This combined product was fractionated and 2.0 g. (12%, n^{25}D 1.6185) of II was collected at 50–55° (0.2 mm.). Several modifications of these conditions failed to result in an increased yield of II.

C. Deacetoxylation of 2-Acetoxybenzo-1,4-oxathiene (IX).—The pyrolysis of IX was carried out at 450–460° in a 20 mm. by 30 cm. Pyrex tube tilted at an angle of 45°. A slow stream of nitrogen was passed through the tube during the reaction. IX (9.7 g., 0.046 mole) in benzene (20 ml.) was passed through the tube at the rate of 20 drops per minute. The dark product was fractionated to give 5.3 g. of II (pale yellow, b.p. 63–65° (0.7 mm.), n^{26}D 1.6168) and 1.7 g. of IX (b.p. 65–115° (0.7 mm.)). II, obtained from IX, was shown to be identical to II, obtained from V and VIII by: (1) comparisons of infrared and ultraviolet spectra; (2) oxidation to the sulfone, m.p. and mixed m.p. 154–155°; and (3) composition (C and H).

Benzo-1,4-oxathiadiene Sulfone (X).—A mixture of II (1.2 g., 0.08 mole), hydrogen peroxide (5 ml. of 30%) and glacial acetic acid (20 ml.) was heated at the reflux temperature for five minutes. An additional 5 ml. of hydrogen peroxide was added and the resulting solution was concentrated to a volume of 5 ml. The yellow solution was diluted with 15 ml. of water and the solid that precipitated from the cold mixture was recrystallized from ethanol. The sulfone melted at 154–155°.

Anal. Calcd. for $C_8H_6SO_3$: C, 52.75; H, 3.32. Found: C, 53.08; H, 3.60.

Benzo-1,4-oxathiene Sulfone (XI).—X (0.80 g., 0.0044 mole), in absolute ethanol (120 ml.), was reduced with hydrogen (50 p.s.i.) using 10% palladium on charcoal (0.3 g.) as catalyst. The catalyst was removed and the ethanol was concentrated to 10 ml. The alcoholic residue was cooled, and 0.53 g. of XI (m.p. and mixed m.p. with an authentic sample[16] was 78.5–80°) was obtained.

Reaction of II with Trinitrobenzene.—A solution containing II (0.85 g., 0.0057 mole), 1,3,5-trinitrobenzene (1.17 g., 0.0055 mole) and 95% ethanol (30 ml.) was heated at the reflux temperature for five minutes. The solution was cooled and 1.06 g. of long red needles (m.p. 92–107°) was obtained. The product melted at 101–104° after several recrystallizations from alcohol. The addition product was not stable—as evidenced by the analyses and the change of color (white edges) upon drying.

Anal. Calcd. for $C_{14}H_9O_7SN_3$: C, 46.29; H, 2.50. Found: C, 46.75; H, 2.75.

Reaction of II with Air.—Samples of benzo-1,4-oxathiadiene (II) have been stored for several months in an atmosphere of nitrogen with no apparent change in appearance or refractive index; however, II reacts with oxygen[17] in the air to give gells. When these gells were treated with ether, or other common solvents, a small amount of material dissolved[18] leaving an insoluble amorphous white solid. This product has the composition calculated for XIV.

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[16] D. Greenwood and H. A. Stevenson, *J. Chem. Soc.*, 1514 (1953), recently reported the conversions III → XII → XI. Our procedures, developed independently, are essentially the same as those reported.

[17] Samples of II showed varying results when exposed to air. Some samples gelled immediately, others required several days, and others, particularly samples prepared from the acetate, one to two weeks.

[18] The small amount of solid, ether-soluble material, was not characterized. It was assumed to be XIII by analogy to the thorough study of the reaction of dimethylketene ethyleneacetal with oxygen. *Cf.* ref. 7.

Anal. Calcd. for $(C_8H_6OS{\cdot}O)_n$: C, 57.81; H, 3.64. Found: C, 58.03; H, 3.82.

Addition of Ethanol to II. A.—A solution of II (2.85 g., (0.0190 mole), $n^{26}D$ 1.6174), ethanol (15 ml.) and 7.5 *N* hydrogen chloride in ethanol (1 ml.) was heated at the reflux temperature for 85 hours. The mixture was then fractionated to give 1.09 g. ($n^{25.7}D$ 1.6167–1.6113) of an oil boiling at 75–97° (1.4–0.9 mm.), and 2.08 g. ($n^{25.7}D$ 1.5726) of an oil boiling at 97–101° (0.9–0.8 mm.). The lower boiling fraction was principally unchanged starting material (38%); the higher boiling fraction was practically pure 2-ethoxybenzo-1,4-oxathiene (V, 55.8%). The acetal V was further characterized by its conversion into VI (m.p. and mixed m.p. 131–132.5°).

B.—Attempts to add ethanol to II under milder conditions[8] failed. Distillation of a mixture prepared from II (2.9 g.), ethanol (10 ml.) and 7.5 *N* hydrogen chloride in absolute ethanol (1/2 ml.), that had been heated at the reflux temperature for four hours and then allowed to stand at room temperature for 24 hours, gave recovered starting material (1.8 g., b.p. 47–51° (0.09 mm.), $n^{25}D$ 1.6141, 62% recovery) and tarry residue (0.9 g., 31%).

2,3-Dibromobenzo-1,4-oxathiene (XV).—Bromine (1.2 g., 0.0075 mole) was added dropwise to a cold (0°), stirred solution of II (1.1 g., 0.0073 mole, $n^{25}D$ 1.6082) in carbon disulfide (5 ml.). When the addition was complete, the carbon disulfide was removed and the residue was recrystallized from petroleum ether. The product (2.0 g., 89%, m.p. 102–104°) melted at 105–106° after several recrystallizations from petroleum ether.

Anal. Calcd. for $C_8H_6OSBr_2$: C, 30.99; H, 1.95. Found: C, 31.31; H, 1.89.

Hydrolysis of 2,3-Dibromobenzo-1,4-oxathiene (XV). 1.—A solution of XV (0.20 g., 0.0065 mole) in 10 ml. of 50% alcohol was heated at the reflux temperature for 15 minutes, and was then combined with 15 ml. of 2,4-dinitrophenylhydrazine reagent.[19] Glyoxal 2,4-dinitrophenylosazone (0.15 g., 55%, m.p. 324–329° dec.) was obtained. This product (m.p. 328° dec. from ethyl acetate) caused no depression in melting point when admixed with a sample of authentic glyoxal 2,4-dinitrophenylosazone (m.p. 328° dec.).

2.—In a similar reaction using phenylhydrazine and one drop of acetic acid, glyoxalosazone (58%, m.p. and mixed m.p. 169–171°) was obtained.

Reaction of II with Nitric Acid.—The nitration of II (3.0 g.) was carried out in acetic acid by the same procedure previously described for the nitration of I.[3] The yellow semisolid became sticky and darkened as it dried; the product completely decomposed to a foamy puff of orange-red tar and oxides of nitrogen when allowed to stand overnight.

Reaction of II with N-Methylformanilide and Phosphorus Oxychloride.—The Vilsmeyer reaction employing II (4.5 g., 0.033 mole) was carried out by a procedure essentially identical to that previously described for I.[3] The crude solid aldehyde weighed 3.2 g. (54%) and melted at 112–125.5°. The product was easily purified by recrystallization from benzene followed by low pressure sublimation. The pure aldehyde was canary-yellow in color and melted at 127–128°.

Anal. Calcd. for $C_9H_6O_2S$: C, 60.68; H, 3.40. Found: C, 60.77; H, 3.68.

The 2,4-dinitrophenylhydrazone of the aldehyde melted at 246–247° (from chloroform-alcohol).

Anal. Calcd. for $C_{15}H_{10}O_5SN_4$: C, 50.28; H, 2.81; N, 15.64. Found: C, 49.89; H, 3.11; N, 15.53.

The *p*-nitrophenylhydrazone of the aldehyde melted at 217–219° (from ethanol).

Anal. Calcd. for $C_{15}H_{11}O_3SN_3$: C, 57.51; H, 3.54. Found: C, 57.46; H, 3.72.

Preparation of Benzo-1,4-dithiadiene (I) by Vapor Phase Dealkoxylation of 2-Ethoxybenzo-1,4-dithiene. 1. At 300°.—The procedure used was essentially that previously described[20] for the dealkoxylation of 2,5-diethoxy-1,4-dithiene. The distilled product (69–71°, 0.12 mm.) contained acid (phenolic odor) products and was purified by extraction with 5% sodium hydroxide and refractionation. There was obtained 5.90 g. (49% yield) of I ($n^{25}D$ 1.6720–1.6749).

2. At 250°.—When the pyrolysis was carried out at 250°, there was obtained 7.2 g. (58% yield) of I ($n^{25}D$ 1.6728) boiling at 80–84° (0.30 mm.).

2,3-Dibromobenzo-1,4-dithiene (XVII).—Bromine (1.21 g., 0.00753 mole) was added dropwise to a cold (0°), stirred solution of benzo-1,4-dithiadiene (I, 1.25 g., 0.00753 mole) in carbon disulfide (10 ml.). Carbon disulfide was removed by distillation on a steam-bath; during the distillation the evolution of hydrogen bromide was quite evident. The dark residue was leached with petroleum ether (60–68°), and the insoluble material was discarded. The petroleum ether fraction (200 ml.) was concentrated to a volume of 10–15 ml. When the concentrated solution was cooled 2.0 g. (81%) of crude XVII (m.p. 100–107° dec.) was obtained. The dibromide was obtained as near white, transparent crystals (m.p. 106–108° dec.) by crystallization from benzene–petroleum ether.

Anal. Calcd. for $C_8H_6S_2Br_2$: C, 29.47; H, 1.86. Found: C, 29.49; H, 1.87.

The dibromide proved to be very unstable and decomposed with loss of hydrogen bromide to a purple solid, even when kept in a refrigerator. The purple solid formed beautiful purple solutions in alcohol, which redeposited the solid when water was added. This product had no definite melting point and has not been identified.

Anal. Found: C, 48.99; H, 2.57.

Attempts to hydrolyse XVII by procedures similar to those described for XV, gave no ketonic derivatives.

Reaction of 2,3-Dibromobenzo-1,4-dithiene (XVII) with Sodium Iodide.—A solution of XVII (0.20 g., 0.00061 mole) in acetone (5 ml.) was combined with 1 g. of sodium iodide in 10 ml. of acetone. The solution was swirled for one minute, 6 drops of 10% sulfuric acid was added, and the solution was titrated with standard sodium thiosulfate. The iodine liberated (0.000645 mole) corresponded to 105% of the theoretical calculated for one molar equivalent of iodine. Benzo-1,4-dithiadiene was isolated as the other product of the reaction, and identified by comparison of its ultraviolet spectrum with an authentic sample.[3]

Reaction of Benzo-1,4-oxathiadiene (II) with 2,4-Dinitrophenylhydrazine. 1. In the Presence of Air.—A solution of II (0.30 g., 0.002 mole) in 15 ml. of 2,4-dinitrophenyl reagent (2 ml. of concd. H_2SO_4, 3 ml. of water, 0.4 g. or 0.002 mole of 2,4-D and 10 ml. of ethanol) was allowed to stand at room temperature in the presence of air. The solution remained clear for one-hour, then glyoxal 2,4-dinitrophenylosazone began to precipitate slowly. The mixture was allowed to stand for ten days, during which time the solid continued to form. The mixture was then heated to boiling and filtered while hot. The glyoxal 2,4-dinitrophenylosazone weighed 0.25 g. (0.00059 mole) and caused no depression in m.p. when admixed with an authentic sample of glyoxal 2,4-dinitrophenylosazone (m.p. 325–328° dec. from nitromethane).

2. In the Absence of Air.—The experiment was conducted as described above, but the reaction mixture was kept in a closed vessel in an atmosphere of nitrogen. The mixture remained essentially clear until the eleventh day, at which time yellow platelets began to separate. Water (15 ml.) was added to the reaction mixture; the precipitate that formed (0.21 g., 0.00060 mole) was identified as VI (m.p. and mixed m.p. 131–133°).

Reaction of VI with 2,4-Dinitrophenylhydrazine.—A solution of 2-hydroxyphenylthioacetaldehyde 2,4-dinitrophenylhydrazone (VI, 0.20 g., 0.00057 mole) in 30 ml. of 95% ethanol containing 8.6 ml. (0.23 g., 0.0012 mole of 2,4-dinitrophenylhydrazine) of 2,4-dinitrophenylhydrazine reagent was allowed to stand at room temperature for 17 days. There was essentially no reaction (a trace of the glyoxal osazone had formed).

When a reaction mixture identical to that described above was heated on a steam-bath for one-hour, and then allowed to stand at room temperature for three days a 17% yield (0.04 g.) of glyoxal 2,4-dinitrophenylosazone formed. When the reaction mixture was heated at the reflux temperature for five days the yield of glyoxal 2,4-dinitrophenylosazone was 62%.

Reaction of the 2,4-Dinitrophenylhydrazones of 2-Hydroxyethyloxyacetaldehyde (XVIIIa) and 2-Hydroxyethyl-

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(19) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(20) W. E. Parham, H. Wynberg and F. L. Ramp, THIS JOURNAL, **75**, 2065 (1953).

thioacetaldehyde (XVIIIb) with 2,4-Dinitrophenylhydrazine. 1.—2,4-Dinitrophenylhydrazine reagent (7.5 ml., 0.20 g. or 0.001 mole of 2,4-DNP) was added to a solution of XVIIIa[21] (0.14 g., 0.00049 mole) in 15 ml. of 95% ethanol, and the resulting solution was allowed to stand at room temperature. The formation of glyoxal 2,4-dinitrophenylosazone was noticed after 2.5 hours. The glyoxal 2,4-dinitrophenylosazone that had formed after five days weighed 0.06 g. (29%). The filtrate continued to deposit XVI.

When a mixture identical to that described above was heated at the reflux temperature for one hour and then allowed to stand for two days at room temperature, the yield of XVI was 73%.

2.—The same experiments described in 1 (above) were repeated using XVIIIb.[21] The yield of glyoxal 2,4-dinitrophenylosazone after five days at room temperature was 6%; after one hour at the reflux temperature followed by two days at room temperature the yield of XVI was 54%.

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[21] W. E. Parham, THIS JOURNAL, **69**, 2449 (1947).

[CONTRIBUTION FROM THE RESEARCH CENTER, THE B. F. GOODRICH COMPANY]

Vinylidene Cyanide. III[1]

BY H. GILBERT, F. F. MILLER, S. J. AVERILL, R. F. SCHMIDT, F. D. STEWART AND H. L. TRUMBULL

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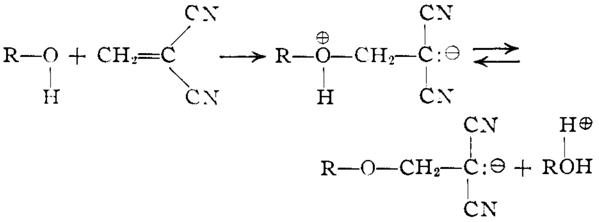
The homopolymerization of vinylidene cyanide proceeds vigorously by an ionic mechanism. Polymerization by free radical initiation is slow. The resulting polymer undergoes carbon chain scission in the presence of moisture.

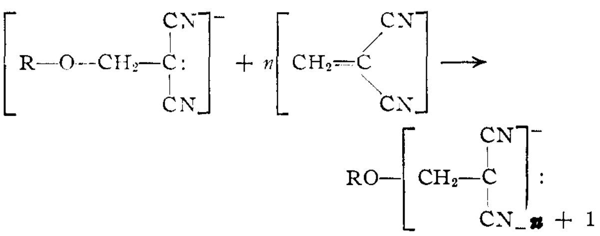
Previous papers in this series[2] describe several syntheses of monomeric vinylidene cyanide, in this paper referred to as $V(CN)_2$. The present paper discusses the homopolymerization of this new monomer.[3]

Ionic Catalysis.—Monomeric $V(CN)_2$ polymerizes in the cold upon contact with water to form a hard, white, infusible resin. In this respect the monomer resembles nitroethylene.[4] The anionic initiation of $V(CN)_2$ proceeds rapidly upon contact with alcohols, amines and ketones and seems to be of the form



$$R{-}\underset{H}{O} + CH_2{=}C(CN)_2 \longrightarrow R{-}\overset{\oplus}{\underset{H}{O}}{-}CH_2{-}C{:}^{\ominus}(CN)_2 \rightleftarrows R{-}O{-}CH_2{-}C{:}^{\ominus}(CN)_2 + \overset{H^{\oplus}}{R}OH$$

with polymerization occurring ionically

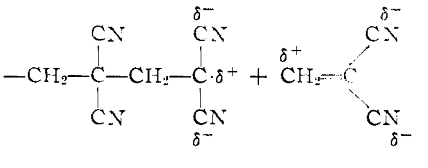


$$\left[R{-}O{-}CH_2{-}C{:}(CN)_2\right]^- + n\left[CH_2{=}C(CN)_2\right] \longrightarrow RO{-}\left[CH_2{-}C(CN)_2\right]^{-}_{n+1}{:}$$

This rapid anionic polymerization of $V(CN)_2$ is attributable to the high electron withdrawal of the nitrile groups.

The water emulsion polymerization techniques commonly used with vinyl monomers have not been successful with authentic $V(CN)_2$ since we have always obtained contact polymerization before the emulsion can be formed.[5] Attempts to prepare copolymers of $V(CN)_2$ in water emulsion have also led to the homopolymeric vinylidene cyanide.

Free-Radical Catalysis.—When attempts are made to homopolymerize $V(CN)_2$ by the usual free-radical initiators, such as benzoyl peroxide or ultraviolet light, the propagation reaction is very slow and very little polymer is formed. The slow rate of addition of $V(CN)_2$ monomer to the radical chain end is probably due to high electrostatic repulsion



$$-CH_2{-}C(CN)_2{-}CH_2{-}C(CN^{\delta-})_2{\cdot}\delta^+ + \overset{\delta^+}{CH_2}{=}C(CN^{\delta-})_2$$

Resonance stabilization of the chain end also contributes to the slow rate of homopolymerization. Early in our work we found that rapid homopolymerization could be achieved with diazo catalysts, such as methoxyphenyldiazothionaphthalene. This, however, is believed to be an ionic polymerization caused by basic atoms in the diazo compound.

Polyvinylidene Cyanide.—The homopolymer is a hard, white, infusible, difficultly soluble resin (density 1.31) which darkens on standing in moist air. Depolymerization to monomer starts at about 160°, and continues at an increased rate as the temperature is raised.[6] No sharp melting point is observed, but X-ray diffraction patterns show some evidence of crystallinity. The polymer is soluble in dimethylformamide, tetramethylene cyclic sulfone, tetramethylurea,[7a] and triethyl phosphate.[7b] It is insoluble in all common solvents such as ketones, alcohols and hydrocarbons. The homo-

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[1] This paper was presented before the Division of Polymer Chemistry at the 124th Meeting of the American Chemical Society in Chicago, Ill., September 7, 1953.

[2] A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart and H. L. Trumbull, THIS JOURNAL, **72**, 1305 (1950); **72**, 3127 (1950).

[3] R. F. Schmidt, A. E. Ardis and H. Gilbert, U. S. Patent 2,589,294 (March 18, 1952); *C. A.*, **46**, 6430b (1952).

[4] H. Wieland and E. Sakellarios, *Ber.*, **52**, 898 (1919).

[5] Compare J. B. Dickey, U. S. Patent 2,466,395 (April 5, 1949); *C. A.*, **43**, 4897c (1949).

[6] A. E. Ardis and H. Gilbert, U. S. Patent 2,535,827 (December 26, 1950); *C. A.*, **45**, 3196b (1951).

[7] (a) A. E. Ardis, U. S. Patent 2,574,369 (November 6, 1951); *C. A.*, **46**, 1812g (1952); (b) R. F. Schmidt, U. S. Patent 2,594,353 (April 29, 1952); *C. A.*, **46**, 7367c (1952).