final mixture effectively brings down the *m*-iodobenzoic acid. The product recovered was recrystallized from glacial acetic acid by diluting the solution with water yielding 18.0 grams (75%) of pure product. M.p. and mixed m.p. 181–183°.

Anal. Calcd. for $C_7H_5O_2I$: 248. Found: Equiv. 246.

DETROIT 1, MICH.

Heterocyclic Vinyl Ethers. XV. The Thermal Stability of 1,4-Dithiadiene and Its Reaction with Chlorine.[1]

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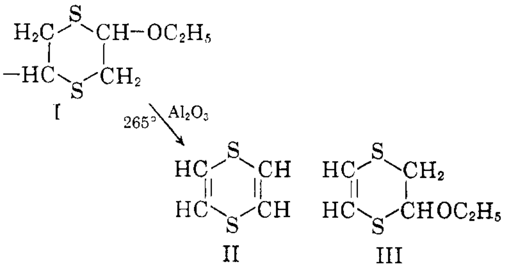
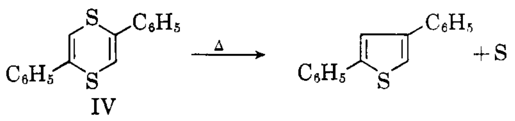
We now wish to report some terminal experiments with the heterocycle 1,4-dithiadiene, including an improved method of synthesis, its thermal stability, and its reaction with chlorine.

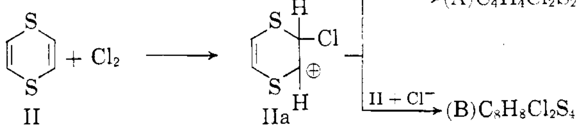
The preparation of 1,4-dithiadiene (II), by the vapor phase dealkoxylation of 2,5-diethoxy-1,4-dithiane (I) on alumina, has been re-examined. The reaction temperature was accurately measured and carefully controlled. Optimum yields of II (47–60%) were obtained when molten I, in the absence of solvent, was reacted on alumina at 260–265°. The use of higher temperatures (310°), as previously reported,[2] gave only viscous oils and neither II nor III could be isolated.



1,4-Dithiadiene was previously reported[2] to decompose at its boiling point (181°/735 mm.). We have subsequently found that the thermal stability of II is quite dependent upon its purity. Pure 1,4-dithiadiene can be distilled at atmospheric pressure under nitrogen with no apparent decomposition. A sample of pure II was maintained at the reflux temperature in a nitrogen atmosphere for 50 minutes with no evidence of decomposition; however, after that time a rapid decomposition initiated. The infrared spectra of the crude decomposition residue, and of the more volatile material obtained from the pyrolysis reaction in the preparation of II, did not reveal bands characteristic of thiophene. Indophenine color tests for thiophene were also negative. Thus, the thermal stability of 1,4-dithiadiene is in contrast with that of 2,5-diphenyl-1,4-dithiadiene (IV). The latter decomposes at 180° to give 68% yields of 2,4-diphenylthiophene and sulfur.[3]

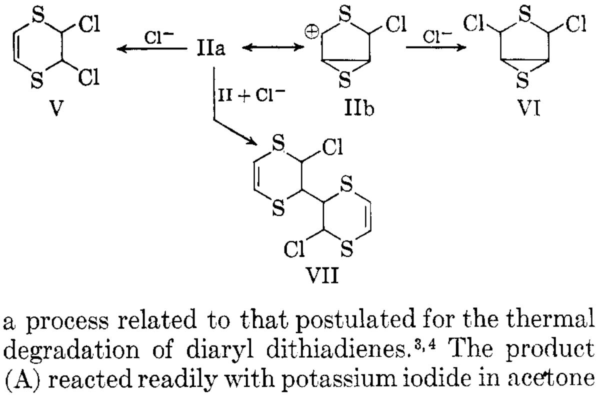


The reaction of 1:4-dithiadiene, in carbon tetrachloride at zero degrees, with one molar equivalent of chlorine, resulted in the formation of two solid products: (A) m.p. 104.5–105.5° (22%), and (B) m.p. 157–158° dec. (29%).



(A) is relatively unstable in air, becoming first brown and then dark purple. Elemental analysis and molecular weight determinations established the molecular formula $C_4H_4Cl_2S_2$. Elemental analysis of (B) gave the empirical formula $C_4H_4ClS_2$, although attempts to determine the exact molecular weight were not successful, because of its very low solubility in suitable solvents at low temperatures, and of its thermal instability at higher temperatures. An approximate value obtained suggested the molecular formula $C_8H_3Cl_2S_4$.

Possible structures for (A) were considered to be V or VI, and for (B) the structure VII, or a product related to VI. Product VI could form, as shown in the above equations (IIa → IIb → VI), a process related to that postulated for the thermal degradation of diaryl dithiadienes.[3,4] The product (A) reacted readily with potassium iodide in acetone to liberate iodine; however, 1,4-dithiadiene disulfone could not be recovered from the acetone solution subsequent to oxidation with hydrogen peroxide. Failure to isolate the disulfone from such mixtures was subsequently shown to be of little



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[1] This work was supported by the Office of Ordnance Research, U. S. Army, Contract No. DA-11-022 ORD 2616.

[2] W. E. Parham, H. Wynberg and F. Ramp, *J. Am. Chem. Soc.*, **75**, 2065 (1953).

[3] W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **76**, 4960 (1954).

[4] W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **77**, 68 (1955).

TABLE I

Ultraviolet Absorption Spectra of Cyclic and Alicyclic Bis-Mercaptoethylenes

Solvent	Compound	λ	ε	λ	ε	λ	ε	ref.
95% Ethanol	*n*-$C_4H_9SCH{=}CHSC_4H_9$-*n*			251	11348	268[a]	6560	5
	cis *t*-$C_4H_9S{-}CH{=}CHS{-}C_4H_9$-*t*	230[a]	5897	250	9192	263[a]	5377	5
	cis *n*-$C_4H_9{-}SCH{=}CH{-}C_4H_9$-*n*	232[a]	5062	257	8474	269	7638	5
	n-$C_4H_9SCH{=}CHSCH_3$	226	5392	252	9717	275[a]	3749	5
	cis $CH_3SCH{=}CHSCH_3$	228	4917	253	9051	270–300[a]		5
	trans $CH_3SCH{=}CHSCH_3$	230	5096	254	8863	270[a]	5143	5
	$C_6H_5SCH{=}CHSC_4H_9$-*n*	217[a]	9924			271	12991	5
	$C_6H_5SCH{=}CHSC_4H_9$-*t*	217[a]	11043			273	14104	5
	n-$C_4H_9SCH{=}CHOC_2H_5$	215	8534	248	3928			5
	t-$C_4H_9SCH{=}CHOC_2H_5$	215	8534	248	3928			5
	1,4-dithiadiene			262	5400	266–270	5280	2
	2,5-dimethyl-1,4-dithiadiene			262	4131	269	4102	7
	2,5-diphenyl-1,4-dithiadiene			259	22100	309	8900	3
	1,4-dithiene					282	4365	6
	bis-1,2(ethylmercapto)cyclohexene			263	4750			
	$C_2H_5SC(CH_3){=}CHSC_2H_5$			225	1730			
	2-methoxy-1,4-dithiene-5	221	3320			272	4580	
	2-ethoxy-1,4-dithiene-5	220				273		
	3-ethoxy-2,5-dimethyl-1,4-dithiene-5	232	4300			268	4000	7
	3-*n*-butoxy-2,5-dimethyl-1,4-dithiene-5	232	4330			268	4080	7
	2,3-dihydro-4H-thiopyran	208	3000	225	4400	247	2200	
Chloroform	2,3-dichloro-1,4-dithiene-5 (V)			243	3784	281	4351	
	Compound VII			245	7429	282	7995	
	2-ethoxy-1,4-dithiene-5			246	5466	275	7076	
	n-$C_4H_9SCH{=}CHSCH_3$					261	2140	
	t-$C_4H_9SCH{=}CHSC_4H_9$-*t*			243[a]	4760	272	7470	

[a] Pt. of inflection.

consequence, for only small yields (<10%) of 1,4-dithiadienedisulfone could be isolated from similar mixtures containing authentic 1,4-dithiadiene and iodine.

More compelling evidence for the structures V and VII was obtained by comparison of their spectra with those of related compounds. The infrared spectrum of (A) (KBr disk) showed characteristic absorption at: 650 cm.$^{-1}$ (strong), 680 cm.$^{-1}$ (strong), 1220 cm.$^{-1}$ (medium) and 1555 cm.$^{-1}$ (strong); the higher melting solid (B) (KBr disk): 645 cm.$^{-1}$ (strong), 665 cm.$^{-1}$ (strong), 680 (in chloroform, weak), 1215 cm.$^{-1}$ (medium), 1550 cm.$^{-1}$ (strong). These spectra were compared with those of seven available compounds (from table I), both cyclic and alicyclic, possessing the group R—S—CH=CH—S—R. These compounds show characteristic absorption in the regions: 670–685 cm.$^{-1}$ (medium to strong), 1212–1240 cm.$^{-1}$ (medium to strong), and 1537–1550 cm.$^{-1}$ (medium to strong). The bands at 1537–1550 cm.$^{-1}$ are not present in compounds with the grouping R—S—CH=CH—OR, but are replaced by new bands at 1615–1620 cm.$^{-1}$ (strong) and 1720–1725 cm.$^{-1}$ (weak); consequently, it was concluded from these comparisons that both products (A) and (B) contained the R—S—C=C—S—R structure, and that V and VII were the most probable structures.

It can be seen from Table I that the absorption observed for V is consistent with the substituted dithiene structure. Furthermore, similar absorption noted for VII, with twice the molar extinction coefficient, establishes the relationship of structures proposed.

Attempts were made to oxidize 1,4-dithiadiene to the monosulfoxide by means of equimolar amounts of 40% peracetic acid,[8] iodosobenzene,[9] and 40% hydrogen peroxide.[10] In all cases only recovered 1,4-dithiadiene was finally obtained. The infrared spectrum of the crude reaction products, however, contained bands which could be associated with the sulfoxide group (1052–1022 cm.$^{-1}$).[11] There was no evidence for the formation of thiophene in these reactions. The oxidation of II with excess hydrogen peroxide readily gives the mono- or disulfone[2] in high yield. Thus, toward oxidation, 1,4-dithiadiene behaves in a manner

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(5) W. E. Parham, R. F. Motter and G. L. O. Mayo, *J. Am. Chem. Soc.*, **81**, 3386 (1959).

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(9) A. H. Ford-Moose, *J. Chem. Soc.*, 2126 (1949).

(10) O. Hinsberg, *Ber.*, **43**, 289 (1910).

(11) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., 295 (1954). (b) Organic Sulfur Compounds, "Infrared Spectra of Organic Sulfur Compounds," N. Kharasch, ed., Vol. 1, Chap. 3, L. J. Bellamy. Pergamon Press Inc. (in press), New York 22, N. Y.

quite different from the diaryl-dithiadienes. 2,5-Diphenyl-1,4-dithiadiene (IV) readily gives a monosulfoxide which decomposes, or is subsequently decomposed,[3] to a thiophene in high yield.

Attempts were made to nitrate 1,4-dithiadiene by the action of nitric acid in acetic acid, cupric nitrate in acetic anhydride, and tetranitromethane. In all cases the final products were tars plus a small amount of amorphous acidic material. There were some indications, however, that unstable intermediates were being formed. In the tetranitromethane reaction a dark red amorphous solid was isolated which rapidly turned a tar.

EXPERIMENTAL

1,4-Dithiadiene (II). The procedure previously described[2] for the conversion of 2,5-diethoxy-1,4-dithiane to 1,4-dithiadiene, by reaction in ethanol with alumina at 310° could not be successfully repeated. The reaction variables were studied and the following procedure was found to afford I in consistent yields of 47–60%.

Alumina pellets (60 g., Harshaw Chemical Co., T 1/8″) were heated for 48 hr. at 310° in a vertical glass tube (2 × 30 cm.). The temperature was lowered to 265° and molten[12] 2,5-diethoxy-1,4-dithiane (36.0 g., 0.173 mole) was passed through the tube at 8 drops per minute with dry nitrogen gas at 0.5 l. per minute, followed by absolute ethanol (10 ml.). The crude product, collected in a dry ice cold trap, was dissolved in ether (150 ml.) and the solution washed with water (10 ml.), saturated sodium chloride (2 × 15 ml.) and dried over magnesium sulfate. Distillation of the product through an 8″ spiral wire column yielded impure 1,4-dithiadiene (12.0 g., 60%), b.p. 77–79°/15 mm., $n_D^{23.6}$ 1.6318. The product was further purified by chromatography as before[2] to give pure 1,4-dithiadiene, b.p. 71.5°/17 mm., $n_D^{25.8}$ 1.6343.

When a saturated ethanolic solution of 2,5-diethoxy-1,4-dithiane was pyrolysed at 260°, only 2-ethoxy-1,4-dithiene-5 (56%) was obtained.

Thermal Stability of 1,4-Dithiadiene. Distillation. A sample of 1,4-dithiadiene (2.0 g., $n_D^{20.7}$ 1.6347) was distilled slowly at atmospheric pressure under dry nitrogen. The distillate was a yellow-orange liquid $n_D^{20.7}$ 1.6348–1.6355 and the residue consisted of a dark red brown tar (0.06 g.).

Refluxing. A 1.0 g. sample could be heated under reflux in the presence of nitrogen for a period of 50 minutes. There was little evidence of decomposition, as indicated by only a slight darkening in color. After this time the material appeared to undergo a sudden decomposition, emitting a cloud of white smoke through the condenser and leaving a black tarry residue, possessing a strong odor of hydrogen sulfide. The reflux condenser was rinsed with thiophene free benzene and the resulting solution tested for thiophene by the indophenine reaction.[13] No blue color could be detected.

During preparation. An attempt was made to isolate any thiophene present in the material obtained as a forerun in the preparation of 1,4-dithiadiene as the 2-chloromercuri-derivative: 0.82 g. of liquid forerun was diluted with ethanol (2 ml.) and treated with 4*M* sodium acetate solution (8 ml.) and 0.25*M* mercuric chloride solution (40 ml.). The dark yellow precipitate thus formed could not be recovered from an aqueous ethanolic solution.

The infrared spectra of crude pyrolyses products did not show any bands which could be used to identify thiophene.

Reaction of 1,4-Dithiadiene with Chlorine. To a solution of 1,4-dithiadiene (11.6 g., 0.1 mole) in carbon tetrachloride (125 ml.) was added, at 0° with stirring, a solution of chlorine (7.1 g., 0.1 mole) in carbon tetrachloride (125 ml.) during one hour. The mixture was stirred at 0° for an additional 15 minutes and then at room temperature for 2 hr. There was filtered off a purple solid (4.41 g., 29% of $C_8H_8Cl_2S_2$), recrystallization of which gave compound B as colorless prisms, m.p. 157–158° (dec.).

Anal. Calcd. for $C_8H_8Cl_2S_4$: C, 31.68; H, 2.66; Cl, 23.38; S, 42.29; mol. wt. 303. Found: C, 31.57; H, 2.57; Cl, 23.24; S, 43.11; mol. wt. 486° (benzene).[14]

The filtrate was evaporated under reduced pressure, and the residue was recrystallized from petroleum ether B to give compound A (V) as colorless needles (4.15 g., 22% of $C_4H_4Cl_2S_2$) m.p. 104.5–105.5°. Compound A slowly decomposed in air and was therefore stored under nitrogen.

Anal. Calcd. for $C_4H_4Cl_2S_2$: C, 25.67; H, 2.15; Cl, 37.90; S, 34.27; mol. wt., 187. Found: C, 25.66; H, 2.07; Cl, 37.66; S, 35.30; mol. wt. (f.p. benzene), 171, 186, 186.

Reaction of Compound A with Sodium Iodide in Acetone. A solution of sodium iodide (4.80 g., 32 mmole) in acetone (10 ml.) was added to a solution of compound A (0.75 g., 4 mmole) in acetone (10 ml.), and the mixture was allowed to stand for periods varying from 30 minutes to 16 hr. The formation of iodine was evident within a few minutes. The solution was diluted with ether (25 ml.) and saturated aqueous sodium chloride (20 ml.), and the resulting mixture treated with aqueous sodium sulfite (5%) until the dark red iodine color was removed. The ether solution was diluted with glacial acetic acid (10 ml.) and 10 ml. of 30% hydrogen peroxide added. The solution obtained was heated at 70° for two days. The precipitate (0.25 g.) was identified as "acetone superperoxide" ($C_6H_6O_4$, m.p. and mixed m.p. 131.5°), formed by reaction of acetone with hydrogen peroxide.[15] 1,4-Dithiadiene disulfone could not be isolated from the filtrate.

Similar reactions were carried out using 1,4-dithiadiene instead of compound A. Iodine, of course, was not formed and 1,4-dithiadiene disulfone[2] was isolated from the final reaction mixture in 39% yield (m.p. 241–242° dec.); however, when iodine was added to the original reaction mixture, the yield of disulfone was very low (<10%).

Attempted Conversion of 1,4-Dithiadiene to the Monosulfoxide or to Thiophene by Oxidation. The procedures used were essentially identical to those previously described for the conversion of 2,5-diphenyl-1,4-dithiadiene to 2,5-diphenyl-1,4-dithiadiene monosulfoxide and to 2,4-diphenylthiophene.[8,3,4] In addition, attempts were made to effect these transformations by oxidation with iodosobenzene.[9] The crude products showed a strong broad infrared absorption band in the region 1022–1052 cm.⁻¹, which suggested the possible presence of sulfoxide.[11] They did not show any infrared absorption characteristic of thiophene, and the indophenine[13] test for thiophene was negative in all cases. When the crude products were processed, only unchanged 1,4-dithiadiene was recovered (16 to 30% yield).

Attempted Nitration of 1,4-Dithiadiene. The procedures used, employing nitric acid in acetic acid,[4,16] cupric nitrate

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[12] Preheating of the diethoxy compound I (~80°) was necessary in order to obtain a homogeneous mixture of its solid and liquid isomers. This was achieved by using an infrared lamp.

[13] H. D. Hartough, "Thiophene and Derivatives," Interscience Publishers Inc., 1952, p. 16.

[14] This molecular weight is based on a freezing point depression of only 0.022°. During the determination, some of the solid came out of solution and, therefore, the value would be expected to be somewhat higher than would have been observed otherwise.

[15] Pastureau, *Comp. rend.*, **140**, 1592 (1905).

[16] W. E. Parham, T. M. Roder and W. R. Hasek, *Comp. rend.*, **75**, 1647 (1953).

in acetic anhydride,[17] and tetranitromethane[18] were similar to those previously reported. In all cases, tars plus small amounts of acidic material were isolated. With tetranitromethane, an amorphous red solid was obtained but this rapidly decomposed.

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(17) A. G. Anderson, J. A. Nelson and J. J. Tazuma, *Comp. rend.*, **75**, 4980 (1953).

(18) G. G. Fritz, Ph.D. Thesis, Univ. of Washington, p. 62 (1956).

Characterization of Several *n*-Alkyl Esters of Gibberellin A_3 and Their Comparative Biological Activity[1,2]

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The gibberellins, metabolic products of the fungus *Gibberella fujikuroi*, some of which are also native to higher plants,[3,4] have been shown to alter markedly plant behavior.[5,6] As with other growth regulators, some derivatives are biologically active. Takahashi, *et al.*[7] reported that the methyl ester of gibberellin A_3 (gibberellic acid) was inactive but did not specify the bioassay used. Esterification of the hydroxyl group of gibberellin A_3 had no significant effect on biological activity, while esterification of the carboxyl group resulted in compounds which were inactive when applied to the leaves but were slightly active when applied to the root medium.[8] The response from root treatment may have resulted from hydrolysis of the ester in the culture solution.

These results prompted further study of the *n*-alkyl esters of gibberellin A_3. The synthesis, physical, and chemical properties, and biological activity of the methyl through the *n*-decyl esters are described in this report.

EXPERIMENTAL

Esterification of the carboxyl group of gibberellin A_3 was accomplished with the appropriate alkyl iodide similar to the procedure described in the Australian patent of Imperial Chemical Industries Limited.[8] A mixture of 1.5 g. of gibberellin A_3, 6.5 g. of anhydrous potassium carbonate, 3.5 ml. of allkyl iodide, and 60 ml. of dry acetone was refluxed at 62° for 48 hr. with mechanical stirring. After esterification the acetone was removed by distillation *in vacuo* and the residue washed with water. The esters were further purified by recrystallization from a mixture of ethyl acetate and benzene. All esters were recrystallized to a constant melting point and subjected to carbon and hydrogen analysis. The chemical and physical properties are given in Table I.

BIOLOGICAL ACTIVITY

The comparative biological activities of the esters of gibberellin A_3 in stimulating germination of lettuce seed in the dark, parthenocarpic growth of tomato ovaries, and stem elongation of the bean were determined.

Solutions were prepared by dissolving the appropriate ester in a few drops of ethanol and diluting to the desired volume with distilled water. One hundred lettuce seeds (var. Grand Rapids) were placed in a Petri dish on Whatman No. 1 filter paper, and 5 ml. of the ester solution (3×10^{-5} M) were added to each dish. Seeds similarly treated with five milliliters of distilled water and a comparable concentration of ethanol were used as a control. Seeds were germinated in an incubator at 26 ± 0.5° for 96 hr. Each treatment was replicated five times and the experiment performed twice. In parthenocarpic fruit growth the esters were applied in lanolin paste in concentrations of 3×10^{-3} to 3×10^{-6} M directly to emasculated ovaries of the Michigan-Ohio Hybrid tomato variety. The diameter of the ovaries was measured 5 days after the treatment. Comparative stimulation of stem elongation was determined with Blue Lake beans. Ten ml. of a 3×10^{-5} or 3×10^{-6} M solution was applied to the epicotyl apex and stem elongation (distance from cotyledon to epicotyl apex) was determined after 48 hr.

Methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, and *n*-heptyl gibberellates significantly increased the per cent of lettuce seed that germinated in the dark (Table I) with the methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl gibberellates equal to or approaching the activity of gibberellin A_3. Germination was not significantly enhanced by the *n*-octyl, *n*-nonyl, or *n*-decyl gibberellates. Parthenocarpic development of tomato ovaries and stem elongation in the bean were not significantly stimulated by any of the esters of the carboxyl grouping of gibberellin A_3. The promotive responses obtained from methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, and *n*-heptyl gibberellates in lettuce seed germination in

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(1) Journal Article No. 2462 from the Michigan Agricultural Experiment Station, East Lansing.

(2) This research was supported by the Horace H. Rackham Research Endowment.

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(8) Pat. Appl. Imperial Chemical Industries, Ltd., Q 11504 A 11656 A Commonwealth of Australia **28.6.55.10190.** (1955).