

## ORGANIC AND BIOLOGICAL CHEMISTRY

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Studies on d-Orbital Conjugation. III. Non-aromaticity of a Derivative of the 1,3-Dithiepinyl Anion, a Ten  $\pi$ -Electron Conjugated System<sup>1</sup>

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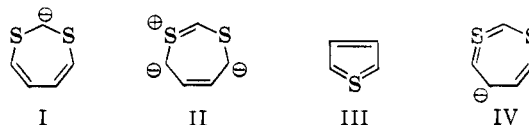
From simple molecular orbital theory it is suggested that aromaticity is expected in a conjugated ring of size  $m$  for all systems of  $4n + 2$   $\pi$ -electrons when  $4n + 2$  is less than  $m$ , but that the extent of the aromatic stabilization should become smaller as  $|4n + 2 - m|$  becomes larger. It is predicted that the aromaticity in a seven-membered ring with ten  $\pi$ -electrons should be considerable, but no special stabilization because of cyclic conjugation was found in a dibenzocarbethoxy derivative of the 1,3-dithiepinyl anion. This result is explained in terms of planarity problems and the charge separation required for delocalization of the  $\pi$ -electrons.

## Introduction

It is often stated<sup>2</sup> that aromaticity is predicted by simple Hückel m.o. theory<sup>3</sup> only for those systems in which a closed shell of electrons in the bonding levels is present. However, one pseudo-experimental criterion for aromaticity is the presence, in a cyclic conjugated system, of greater stabilization by  $\pi$ -electron delocalization than is present in an open-chain analog with the same conjugated elements; with this definition a wider range of aromatic systems is predicted. In Fig. 1 is plotted the predicted cyclic advantage in delocalization energy for several systems as a function of the number of  $\pi$ -electrons in the system. It is seen that both the cyclobutenyl dication and the cyclobutenyl dianion are predicted to be aromatic on this basis; clearly *both* systems cannot have a closed bonding shell configuration, but with our present definition of aromaticity we must consider the open-chain analogs butenyl dication and dianion, as well as the cyclic system. When such calculations are made for other ring systems the same pattern emerges, and two others are also plotted in Fig. 1. For a ring of  $m$ -carbons, compared to an open chain of the same number, no cyclic advantage is found for either 0 or  $2m$   $\pi$ -electrons, in which only one resonance form is possible. Between those limits, all systems of  $4n + 2$   $\pi$ -electrons are maxima, and all  $4n$  systems are minima, but the heights of the maxima for the  $4n + 2$  systems decrease the further they are from the midpoint, i.e., from  $m$ . For a four-carbon system, the magic numbers 2 and 6 would be predicted to be equally good, being equidistant from 4, while the same is found in the eight-carbon case for 6 and 10 electrons; the latter is of course cyclooctatetraenyl dianion.<sup>4</sup>

We wish to focus attention on the predicted aromatic system with ten electrons in a seven-membered ring. Although a cycloheptadienyl trianion would be rather unstable for electrostatic reasons, and attempts to reduce heptaphenylcycloheptatrienyl monoanion<sup>5</sup> further lead to fragmentation of the ring,<sup>6</sup> the electrons could be introduced with heteroatoms such as nitrogen or sulfur. Allinger has prepared several systems of this type using nitrogen,<sup>7</sup> and the available evidence indicates that they are not aromatic. This can be seen to be no contradiction of the theory outlined

above when it is realized that electron delocalization in heterocyclics requires charge separation. Thus for the 1,3-dithiepinyl anion (I) which we wish to consider here, the valence-bond structures utilizing only p-orbitals which distribute the charge are types such as II with charge separation so serious that the electrons may remain essentially localized; the same is true for the valence-bond structures of Allinger's heterocyclic compounds. However, it has been suggested<sup>8</sup> that sulfur resembles a carbon-carbon double bond in possessing both a donor p-orbital and an acceptor d-orbital, and that structure III contributes in thiophene. If the d-orbital can be utilized significantly in this way, structures such as IV can be written for our anion, and this sulfur system may thus still be aromatic.<sup>9</sup>



**Methods and Results.**—In order to examine this question it was decided to determine the rates of base-catalyzed exchange of a series of deuterated esters V-X. These compounds were prepared in a straightforward manner by reaction of the appropriate thiol or phenol with ethyl deuteriodibromoacetic ester. The corresponding hydrogen compounds were also prepared by using undeuterated ethyl dibromoacetate, but in many cases it proved inconvenient to prepare the deuterio compounds from the protonated materials by direct exchange. The kinetic measurements were performed directly in a specially constructed thermostated infrared cell with calcium fluoride windows. The temperature inside the cell was accurately measured. The system examined was 0.2 *M* substrate in carbon tetrachloride-ethanol (9:1 by volume) which was 0.4 *M* in diethylamine. The infrared spectrum was periodically examined between 2600 and 2500  $\text{cm}^{-1}$  for the development of O-D absorption, and the extent of exchange was calculated by comparison of the observed transmittance with that of standard samples, prepared by the addition of known amounts of  $\text{D}_2\text{O}$ . The resulting data gave good first-order kinetics, and the observed pseudo first-order rate constants at  $29.5 \pm 0.5^\circ$  are listed in Table I.

It is apparent that little difference is found between the rates of exchange of any of the compounds listed. If the exchange rate were a valid indication of the stability of the enolate ion, then this would suggest that there is little difference in the stabilities of the anions

(1) This work was supported by grants from the National Science Foundation and the Sloan Foundation. A preliminary report on these results was presented at the 17th National Organic Chemistry Symposium, Bloomington, Ind., 1961.

(2) Cf. M. E. Vol'pin, *Uspekhi Khim.*, **29**, 298 (1960).

(3) For a discussion, cf. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter X.

(4) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); T. J. Katz, W. H. Reinmuth and D. E. Smith, *ibid.*, **84**, 802 (1962).

(5) R. Breslow and H. W. Chang, *ibid.*, **84**, 1484 (1962).

(6) R. Breslow and H. W. Chang, unpublished work.

(7) N. L. Allinger and G. A. Youngdale, *J. Am. Chem. Soc.*, **84**, 1020 (1962); *J. Org. Chem.*, **25**, 1509 (1960).

(8) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1778 (1939); H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949); cf., however, H. H. Jaffé, *J. Phys. Chem.*, **68**, 185 (1954).

(9) For a system with similar problems and possibilities, cf. C. G. Krespan, *J. Am. Chem. Soc.*, **83**, 3434 (1961).

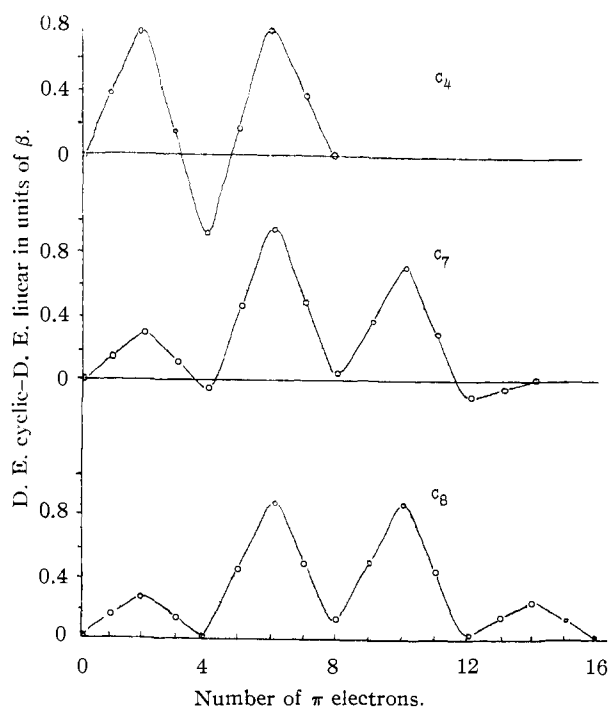


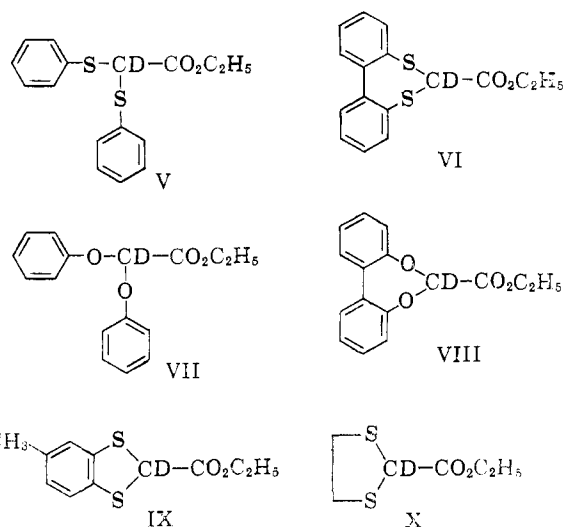
Fig. 1.—Difference in pi electron delocalization energies (from a Hückel calculation) between cyclic and linear simple conjugated systems as a function of the number of pi electrons.

derived from any of these compounds, and in particular that VI and VIII do not exhibit the higher rates which might be expected if their ten  $\pi$ -electron anions are particularly stable. Unfortunately the kinetic method used was sufficiently imprecise that it proved impossible to obtain the activation energies, from the temperature dependence of the rate constants, with any precision. However, even this extra data would not remove the uncertainty which accompanies the interpretation of rate measurements, and therefore it was decided to determine the relative acidities of a cyclic compound and its open-chain analog by direct equilibration.

The two compounds selected for study were V and VI, since they are close analogs whose anions would exemplify the difference between linear and cyclic conjugation, in a seven-atom ten  $\pi$ -electron system, which is of interest. Each of the compounds (with deuterium on the  $\alpha$ -carbon) was treated separately with one equivalent of lithium triphenylmethyl in ether, and each rapidly formed its enolate ion, as evidenced by the incorporation of one proton on the  $\alpha$ -carbon on HCl quenching of the solution. The analysis was performed with n.m.r., using electronic integration. When an equal mixture of the two compounds was treated with two equivalents of lithium triphenylmethyl, quenching produced both protonated compounds in equivalent yield, showing that there is no preferential destruction of either material under these conditions. Then the anion of the open chain ester V was prepared with one equivalent of lithium triphenylmethyl, and one equivalent of (deuterio) VI was added. After standing, the solution was quenched and it was found that a total of one proton had been incorporated, as expected, but that the ratio was 5:1 in favor of the open chain compound V. The same result was obtained when the reaction was carried out with the reverse order of addition of the esters, so a true equilibrium has been reached between their lithium salts. Thus at equilibrium the open-chain compound V is actually somewhat more acidic than is the cyclic

TABLE I  
PSEUDO FIRST-ORDER RATE CONSTANTS FOR DEUTERIUM EXCHANGE AT  $29.5 \pm 0.5^\circ$

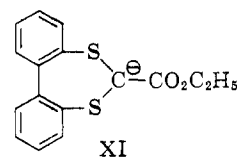
Compound	$k_1 \times 10^3$ , min. <sup>-1</sup>	$\bar{k}_1$	Compound	$k_1 \times 10^3$ , min. <sup>-1</sup>	$\bar{k}_1$
V	3.79	3.90	IX	3.24	3.27
	4.19			3.21	
	3.72			3.37	
VI	2.87	2.86	X	8.11	7.79
	2.86			7.63	
VII	1.85	1.86		7.63	
	1.87				
VIII	2.32	2.34			
	2.37				



compound VI; this is also consistent with the kinetic observations. Accordingly, no aromaticity has been detected in the cyclic ten  $\pi$ -electron anions derived from either VI or VIII.

**Discussion.**—Unfortunately, several explanations are available of our finding that XI is not aromatic. One difficulty is steric in origin. X-Ray studies have shown that the dithiadene ring is non-planar<sup>10</sup> and while this may in part be due to the instability of a cyclic six-membered eight  $\pi$ -electron system, it may be that two sulfur atoms are too large for strainless inclusion in a planar six-membered ring. Then a seven-membered ring species such as I is even less likely to be planar. Furthermore, the particular system chosen is not the ideal one for the detection of a *small* aromatic effect. The presence of the two fused benzene rings on our dithiepinyl anion should diminish the effect, and the carboxylic ester substituent which makes the anion attainable makes it by the same token less susceptible to further stabilization. However, it seems to us that these factors alone do not explain the observations.

The prediction that a seven-membered ring will be more stabilized by delocalization of ten  $\pi$ -electrons than will an open-chain analog is probably correct, although of course there is no evidence yet to support this. The most likely difficulty is the requirement of extreme charge-separation for electron delocalization in heterocyclic systems such as XI. Apparently the hoped-for



(10) P. A. Howell, R. M. Curtis and W. N. Lipscomb, *Acta Cryst.*, **7**, 498 (1954).

d-orbital participation by sulfur has not solved this problem.

### Experimental<sup>11</sup>

**Ethyl Bis-(phenylmercapto)-acetate.**—To a mixture of 100 ml. of benzene and 12.0 g. of NaH (53% in mineral oil) with stirring in nitrogen atmosphere at room temperature was added 27.0 g. of thiophenol over a period of 20 minutes. After the addition was complete, the mixture was heated at 60–70° for 2 hours; there was then added at room temperature 20.5 g. of ethyl dichloroacetate over a period of 20 minutes. This was stirred at room temperature for 1 hour, then at 60–65° for 2 hours. The formed NaCl was separated by filtration. The solvent was removed under reduced pressure and the compound was purified by distilling under high vacuum; b.p. 175–178° at 0.5 mm., yield 14.4 g. (39%). To the product was added *n*-pentane in order to remove the mineral oil. After decantation of the *n*-pentane, the product was redistilled; b.p. 175–177° at 0.5 mm. The infrared spectrum showed strong C=O stretching at 1750 cm.<sup>-1</sup>. The n.m.r. for ethyl bis-(phenylmercapto)-acetate in CCl<sub>4</sub> solution showed a multiplet for phenyl protons at 2.8  $\tau$ , singlet for CH proton at 5.3  $\tau$ , quartet for CH<sub>2</sub> protons at 6.0  $\tau$  and triplet for CH<sub>3</sub> protons at 8.9  $\tau$ . The relative peak areas observed were 10:1:2:3.

*Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub>: C, 63.12; H, 5.29. Found: C, 63.36; H, 5.36.

**Ethyl Bis-(phenylmercapto)-acetate-2-d (V).**—Under nitrogen atmosphere, to a mixture of 0.25 g. of NaH (53% in mineral oil) and 20 ml. of benzene, 1.8 g. of ethyl bis-(phenylmercapto)-acetate was added at room temperature with stirring. The mixture was stirred at room temperature for 1.5 hours, then at ice-bath temperature 1 ml. of D<sub>2</sub>O (99.8%) was added and the mixture was stirred 15 minutes after the addition. The solution was neutralized with 1 *N* HCl and 20 ml. of ether was added. The ether solution was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The product was distilled under high vacuum. The n.m.r. spectrum was taken in CCl<sub>4</sub> solution and the n.m.r. spectrum of the deuterated compound was compared with the spectrum of the undeuterated compound. The n.m.r. indicated that the compound was 75% deuterated. No C–D bond absorption was detected in the infrared spectrum.

**Preparation of Ethyl Diazoacetate-d.**—To 17 g. of ethyl diazoacetate 12 g. of D<sub>2</sub>O (99.8%) was added and the mixture was shaken at room temperature for 48 hours. After this period the D<sub>2</sub>O was separated and the ethyl diazoacetate-d was diluted with 30 cc. of ether. The ether solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and solvent removed under reduced pressure. This crude product was used without further purification; yield 15.0 g. (88%). The infrared spectrum showed characteristic changes at 3030 and at 1265 cm.<sup>-1</sup>. The n.m.r. spectrum showed that 85% of the ethyl diazoacetate-d was present. The 48-hour equilibration time is the optimum for the preparation of ethyl diazoacetate-d. Shorter time decreased the deuterated ester concentration, and increasing the time decreased the yield, because of partial decomposition of the deuterated ester. Similarly, the yield decreased at higher temperature than 25°.

**Ethyl Dibromoacetate-d.**—Ethyl diazoacetate-d (16.8 g.) was dissolved in 30 ml. of CCl<sub>4</sub> and at ice-bath temperature with effective stirring 24 g. of bromine in 50 ml. of CCl<sub>4</sub> was added to the solution over a period of 1 hour. The reaction was very exothermic. In the presence of excess bromine, the color of the solution changed. After the addition was complete, the mixture was stirred at room temperature for 30 minutes. The solvent was removed under reduced pressure and the product was purified by distilling *in vacuo*; b.p. 92–94° at 18 mm., yield 26 g. (72%). The n.m.r. spectrum showed that 85% of the ethyl dibromoacetate-d was present.

**2-Carbethoxydibenzo[d,f][1,3]-dithiepin.**—Under nitrogen atmosphere, to a mixture of 60 ml. of toluene, 2 ml. of dimethoxyethane and 4.01 g. of NaH (53% in mineral oil), 10.5 g. of 2,2'-biphenyldithiol<sup>12</sup> was added with stirring at room temperature over a period of 10 minutes. The mixture was heated at 50–60° for 2 hours. Then 7.5 g. of ethyl dichloroacetate in 10 ml. of toluene was added at room temperature over a period of 15 minutes. After the addition was complete, the mixture was heated at 50–56° for 14 hours, then was cooled at room temperature and 30 ml. of water added. The organic solution was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The product was distilled *in vacuo*, b.p. 177–178° at 0.3 mm. (bath temp.), yield 4.5 g. (33%). The infrared spectrum showed strong C=O stretching at 1750 cm.<sup>-1</sup>. The compound crystallized on standing, and was recrystallized

from ethanol; m.p. 73–74°. The n.m.r. for 2-carbethoxydibenzo[d,f][1,3]-dithiepin in CCl<sub>4</sub> solution was: multiplet for phenyl protons at 2.7  $\tau$ , singlet for CH proton at 4.85  $\tau$ , quartet for –CH<sub>2</sub> protons at 5.85  $\tau$ , and triplet for –CH<sub>3</sub> protons at 8.8  $\tau$ . The relative peak areas observed were 8:1:2:3.

*Anal.* Calcd. for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C, 63.55; H, 4.66. Found: C, 63.84; H, 4.89. Crystallized: Found: C, 63.36; H, 4.58.

**2-Carbethoxydibenzo[d,f][1,3]-dithiepin-2-d (VI)** was prepared in the same way as above. After addition of ethyl dibromoacetate-d, the mixture was stirred at 50–60° for 5 hours. The formed NaBr was separated by filtration and the solvent was removed under reduced pressure. The 2-carbethoxydibenzo[d,f][1,3]-dithiepin-2-d was purified by distillation under high vacuum.

**Ethyl Diphenoxyacetate.**<sup>13</sup>—To a mixture of 100 ml. of benzene and 11.3 g. of NaH (53% in mineral oil) (the NaH was washed with *n*-pentane in order to eliminate the mineral oil), 23.5 g. of phenol was added with stirring over a period of 10 minutes. The mixture was heated at 60–70° for 2 hours, then 19.6 g. of ethyl dichloroacetate in 60 ml. of benzene was added over a period of 10 minutes. The mixture was stirred at 60–70° for 17 hours. Water was added to the mixture and the organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent evaporated under reduced pressure. The product was treated with *n*-pentane in order to eliminate the mineral oil. The product was purified by distillation under high vacuum; b.p. 155–157° at 1.5 mm., b.p. 207–209° at 29 mm.; reported<sup>13</sup> b.p. 208° at 28 mm., yield 7.6 g. (22%). The infrared spectrum showed strong C=O stretching at 1750 cm.<sup>-1</sup>; ultraviolet  $\lambda_{\text{max}}$  265 m $\mu$ ,  $\epsilon$  2,000.

**Ethyl Diphenoxyacetate-2-d (VII).**—Under nitrogen atmosphere, to a mixture of 2.5 ml. of dimethoxyethane, 60 ml. of toluene and 4.4 g. of NaH (53% in mineral oil), 9.4 g. of phenol was added with stirring at room temperature over a period of 20 minutes. The mixture was heated and stirred at 50–60°; then, at room temperature, 12.3 g. of ethyl dibromoacetate-d in 5 ml. of toluene was added over a period of 10 minutes. After heating at 50–60° for 4 hours, the mixture was cooled to room temperature and the formed NaBr was separated by filtration. The solvent was removed under reduced pressure and the product was separated by distillation under high vacuum; b.p. 148–150° (1.7 mm.), yield 1.8 g. (14%). The infrared spectrum did not show C–D stretching. The n.m.r. spectrum showed that 60% of the deuterated ethyl diphenoxyacetate-2-d was present.

**2-Carbethoxydibenzo[d,f][1,3]-dioxepin.**—Under nitrogen atmosphere, to a mixture of 60 ml. of dimethoxyethane, 10 ml. of toluene and 4.5 g. of NaH (53% in mineral oil) 9.2 g. of 2,2'-dihydroxydiphenyl was added with stirring and cooling. The reaction mixture was stirred at room temperature for 15 minutes, then at 50–60° for 2 hours. Then 12.3 g. of ethyl dibromoacetate in 10 ml. of toluene was added at room temperature. The mixture was heated at 50–60° for 16 hours. The formed NaBr was separated by filtration and the solvent was removed under reduced pressure. The compound was purified by distilling under reduced pressure; b.p. 165–170° at 0.7 mm., yield 1.2 g. (9.2%). The infrared spectrum showed strong C=O stretching at 1750 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>: C, 71.16; H, 5.22. Found: C, 71.58; H, 5.38.

The 2-carbethoxydibenzo[d,f][1,3]-dioxepin-2-d (VIII) was prepared in the same way as above using ethyl dibromoacetate-d.

**2-Carbethoxy-5-methyl-1,3-benzodithiole.**—Under nitrogen atmosphere with stirring, to a mixture of 90 ml. of toluene, 10 ml. of dimethoxyethane and 5.6 g. of NaH (53% in mineral oil; the NaH was washed with *n*-pentane in order to eliminate the mineral oil) at room temperature, 10.0 g. of 1,2-mercapto-4-methylbenzene was added over a period of 15 minutes. The mixture was stirred at 60–65° for 2 hours, then 6.1 g. of ethyl dichloroacetate in 20 ml. of toluene was added at room temperature. After the addition was complete, the mixture was stirred at 60–65° for 17 hours. It was then cooled to room temperature and 60 ml. of water and 40 ml. of ether was added. The organic solution was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure; b.p. 144–147° at 0.5 mm., yield 3.5 g. (23%). The infrared spectrum showed strong C=O stretching at 1750 cm.<sup>-1</sup>. The n.m.r. showed a multiplet for phenyl protons at 3.1  $\tau$ , a singlet for CH at 4.8  $\tau$ , a quartet for CH<sub>2</sub> at 5.9  $\tau$ , a singlet for CH<sub>3</sub> at 7.8  $\tau$ , and a triplet for CH<sub>3</sub> at 8.5  $\tau$ . The relative peak areas observed were 3:1:2:3:3.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub>: C, 54.97; H, 5.01. Found: C, 55.24; H, 5.20.

By a similar procedure, using ethyl dibromoacetate-d, the 2-deuterioester IX was prepared; by n.m.r. analysis the compound was 75% deuterated.

**Ethyl Ethylenedisulfoacetate-2-d (X).**<sup>14</sup>—Under nitrogen atmosphere, to 60 ml. of alcohol, 3.9 g. of metallic potassium was

(11) All infrared and n.m.r. spectra are in solution in CCl<sub>4</sub> or CHCl<sub>3</sub>; an internal reference of tetramethylsilane was used for the n.m.r. spectra, which were obtained on a Varian Model A-60 instrument.

(12) H. J. Barber and S. Smiles, *J. Chem. Soc.*, 1141 (1928).

(13) Modification of K. Auwers and K. Hayman, *Ber.*, **27**, 2797 (1894).

(14) G. C. Chakravarty and J. M. Saha, *J. Indian Chem. Soc.*, **5**, 453 (1928).

added in small portions over a period of 20 minutes. With stirring, 9.4 g. of ethylene dithiole was added to the mixture at room temperature over a period of 30 minutes. After the addition was complete, the mixture was heated at 50–56° for 1 hour, then at room temperature 24.5 g. of ethyl dibromoacetate-*d* in 10 ml. of ethanol was added. After refluxing for 5 hours, the formed KBr was separated by filtration and the solvent was removed under reduced pressure. To the residue 40 ml. of benzene was added and the solution was washed with 20 ml. of water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent removed under reduced pressure. The compound was distilled *in vacuo*; b.p. 140–143° at 0.52 mm., yield 1.5 g. (8.3%). The infrared spectrum showed strong C=O stretching at 1750 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>6</sub>H<sub>9</sub>DO<sub>2</sub>S<sub>2</sub>: C, 40.18; H, 6.18. Found: C, 39.89; H, 5.99.

Similarly, the undeuterated ethyl ethylenedisulfidoacetate was prepared using ethyl dibromoacetate.

**Ethyl Bis-(ethylmercapto)-acetate-2-*d* (XI).**—Under nitrogen atmosphere, to a mixture of 80 ml. of toluene and 4.5 g. of NaH (53% in mineral oil) 6.2 g. of ethyl mercaptan was added at room temperature with stirring over a period of 10 minutes. The reaction mixture was heated at 45–50° for 2 hours, then 12.3 g. of ethyl dibromoacetate-*d* in 10 ml. toluene was added at room temperature over a period of 15 minutes. The mixture was then heated at 50–60° for 5 hours. The formed NaBr was separated by filtration. Solvent was removed under reduced pressure and the product was purified by distillation under high vacuum; b.p. 87–89° (0.25 mm.), yield 1.5 g. (15%). The infrared spectrum showed strong C=O stretching at 1750 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>8</sub>H<sub>15</sub>DO<sub>2</sub>S<sub>2</sub>: C, 45.85; H, 8.18. Found: C, 45.84; H, 7.90.

**Stability of 2-Carboxy-5-methyl-1,3-benzodithiole.**—2-Carboxy-5-methyl-1,3-benzodithiole (0.48 g.) was dissolved in a mixture of 1 ml. of ethanol and 9 ml. of CCl<sub>4</sub> and 0.04 ml. of triethylamine (0.4 mole/l.) was added to the reaction mixture at room temperature. The mixture was allowed to stand at room temperature for 24 hours. After this period, 10 ml. of ether was added and the mixture was neutralized with 2 N HCl. The ether solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was distilled under high vacuum; b.p. 134–136° at 0.2 mm., yield, 0.46 g. The infrared spectrum of the product was identical with the infrared spectrum of 2-carboxy-5-methyl-1,3-benzodithiole. Therefore the compound is stable under these conditions.

**Equilibration of the Anions Derived from V and VI.**—For the equilibration experiments "completely deuterated" V was prepared by dissolving 3.0 g. of the undeuterated ester in a solution of 5 ml. of dry dimethoxyethane, 3 ml. of 99.8% D<sub>2</sub>O and 1 ml. of triethylamine. After 3 hours standing at room temperature the solvents were removed *in vacuo*, and the residual V was pumped for 12 hours at 0.1 mm. The infrared spectrum showed this to be pure V, and in the n.m.r. the spectrum was identical with that of previously distilled and analyzed materials except that the signal at 5.3 τ for the α-hydrogen was missing. In a similar fashion "completely deuterated" VI was prepared. These samples were used for the experiments described below.

**Reaction of V with Lithium Triphenylmethyl Followed by 2 N HCl Quenching.**—Under a nitrogen atmosphere, to 30 ml. of lithium triphenylmethyl<sup>18</sup> in ether (0.017 mmole/ml.), 0.152 g. (0.5 mmole) of ethyl bis-(phenylmercapto)-acetate-2-*d* in 5 ml. of anhydrous ether was added with stirring. The red color of the lithium triphenylmethyl disappeared after the addition of the deuterated ester. The mixture was stirred at room temperature for 15 minutes, then the clear solution was added to 10 ml. of 2 N HCl with effective stirring. The ether solution was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent removed under reduced pressure. The n.m.r. in CCl<sub>4</sub> solution indicated

the presence of the α-hydrogen atom at 5.3 τ. The relative peak areas observed were 1:2 for CH:CH<sub>2</sub>.

When the reaction was repeated with 15 ml. of lithium triphenylmethyl (0.017 mmole/ml.) and 0.152 g. of ethyl bis-(phenylmercapto)-acetate-2-*d* was added, after work-up the n.m.r. indicated the presence of the α-hydrogen atom at 5.3 τ. The relative peak areas observed were 0.5:2 for CH:CH<sub>2</sub>.

**Reaction of VI with Lithium Triphenylmethyl Followed by 2 N HCl Quenching.**—Under a nitrogen atmosphere, to 30 ml. of lithium triphenylmethyl (0.017 mmole/ml.), 0.151 g. (0.5 mmole) of 2-carboxy-dibenzo[d,f][1,3]-dithiepin-2-*d* in 5 ml. of anhydrous ether was added with stirring. The red color of the lithium triphenylmethyl disappeared after the addition of the deuterated ester. The mixture was stirred at room temperature for 15 minutes, then the clear solution was added to 10 ml. of 2 N HCl, with effective stirring. The ether solution was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent removed under reduced pressure. The n.m.r. in CCl<sub>4</sub> solution indicated the presence of the α-hydrogen atom at 4.85 τ. The relative peak areas observed were 1:2 for CH:CH<sub>2</sub>.

When the reaction was repeated with the same quantities as above, but after the deuterated ester addition, the mixture was stirred at room temperature for 30 minutes; after work-up as described previously, the n.m.r. in CCl<sub>4</sub> solution indicated the presence of an α-hydrogen atom at 4.85 τ. The relative peak areas observed were 1:2 for CH:CH<sub>2</sub>.

**Equilibrium Study.**—A. Under a nitrogen atmosphere, to 60 ml. of lithium triphenylmethyl (0.017 mmole/ml.) with stirring, a mixture of 0.151 g. (0.5 mmole) of 2-carboxy-dibenzo[d,f][1,3]-dithiepin-2-*d* and 0.152 g. (0.5 mmole) of ethyl bis-(phenylmercapto)-acetate-2-*d* in 10 ml. of anhydrous ether was added. The red color of the lithium triphenylmethyl disappeared after the addition of the deuterated ester. The mixture was stirred at room temperature for 15 minutes, then the clear solution was added to 10 ml. of 2 N HCl with effective stirring. The ether solution was separated and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent removed under reduced pressure. The n.m.r. spectrum showed the presence of α-hydrogen atoms at 4.85 and 5.3 τ. The relative peak areas observed were 2:4 for (CH)<sub>2</sub>:(CH<sub>2</sub>).

B. Under a nitrogen atmosphere, to 30 ml. of lithium triphenylmethyl (0.017 mmole/ml.) with stirring, 0.152 g. (0.5 mmole) of ethyl bis-(phenylmercapto)-acetate-2-*d* in 10 ml. of anhydrous ether was added. The red color of the lithium triphenylmethyl disappeared after the addition of the deuterated ester. The mixture was stirred at room temperature for 5 minutes, then 0.151 g. (0.5 mmole) of 2-carboxy-dibenzo[d,f][1,3]-dithiepin-2-*d* in 5 ml. of anhydrous ether was added, and was stirred for 20 minutes. The equilibrated mixture of the esters then was added to 10 ml. of 2 N HCl with effective stirring. The ether solution was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and removed under reduced pressure. The mixture was analyzed by means of n.m.r. spectroscopy, which showed the presence of the α-protons at 4.85 and at 5.3 τ. A total of one proton had been incorporated and was distributed 16:84% between 2-carboxy-dibenzo[d,f][1,3]-dithiepin and ethyl bis-(phenylmercapto)-acetate.

C. Under a nitrogen atmosphere, to 30 ml. of lithium triphenylmethyl (0.017 mmole/ml.), 0.151 g. (0.5 mmole) of 2-carboxy-dibenzo[d,f][1,3]-dithiepin-2-*d* in 5 ml. of anhydrous ether was added with stirring. The red color of the lithium triphenylmethyl disappeared after the addition of the deuterated ester. The mixture was stirred at room temperature for 5 minutes, then 0.152 g. (0.5 mmole) of ethyl bis-(phenylmercapto)-acetate-2-*d* in 5 ml. of anhydrous ether was added and stirred for 20 minutes. The equilibrated mixture then was added to 10 ml. of 2 N HCl with effective stirring. The ether solution was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent removed under reduced pressure. The n.m.r. spectrum showed the presence of the α-hydrogen atoms at 4.85 and at 5.3 τ. A total of one proton had been incorporated and distributed 16:84% between 2-carboxy-dibenzo[d,f][1,3]-dithiepin and ethyl bis-(phenylmercapto)-acetate.

(15) A. V. Grosse, *Chem. Ber.*, **59**, 2652 (1926).