led us to the conclusion that every coupling constant must be a multiple of this value. This also means that many of the lines will overlap each other.

The interpretations were checked by calculation of the theoretical spectrum. Fig. 3 shows the "stick" spectra of a) half of the experimental and b) half of the calculated spectrum. The coupling constants and the spin density values are listed in the same figure. According to Bowers[4] the odd electron of the anion radical of a monosubstituted benzene nucleus would, if the substituent were electron with-drawing, prefer the symmetric energy level. The average coupling constant of the ortho- and meta-protons is in this case one third of the coupling constant of the para-proton; this result agrees well with the theoretical model of Bowers. The spin density values are calculated using the value −23.8 for Q. The sum of the experimental spin densities is 1.218, consequently there may be regions in the molecule were the spin density is negative.[5] Agreement between the calculated and experimental spectra is good, and one must conclude that the anion radical of trans-1-phenyl-1-propene is the responsible species.

We have carried out a variety of calculations using the HMO method. The difficult question in these calculations is how to treat the perturbing methyl group in the side chain. Use of the inductive model[6] and the heteroatom model[7] did not give satisfactory results. This is in fact not surprising since the HMO method does not take the configuration interaction into consideration. Combining the theory with our experimental results will, as we hope, give parameters which may be useful in other molecules of the same class. The work is continued in this field.

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The Formation of 3,3'-Thenil in the Reaction Between 3-Thienyl-lithium and Dimethyl Oxalate at −70°

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Aromatic 1,2-diketones are usually prepared in high yield through condensation of aromatic aldehydes in the presence of cyanide ion and subsequent oxidation of the resulting benzoin.[1,2] However, the condensation of heterocyclic aldehydes is often an exception. Thus 2-thiophene aldehyde is condensed to 2,2'-thenoin in 30 % yield[3,4] and similar results are observed with the 3-thiophene aldehyde.[5] Since the aldehydes are not always easily accessible the overall yields in preparing the thenils are rather poor.[6] We now report a new way to the thenils.
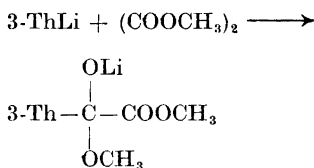
3-Thienyllithium, prepared from ethyllithium and 3-bromothiophene,[7] cooled to −70°, was dropwise added to an equivalent amount of dimethyl oxalate in ether at −70°. After work-up the NMR spectrum of the crude reaction residue

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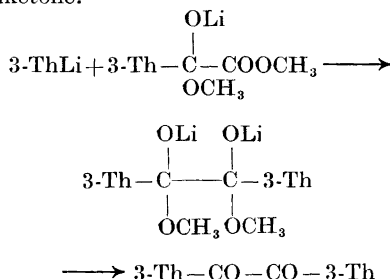
was recorded. No signals for the protons in COOCH$_3$ could be detected. The reaction product was dissolved in warm carbon tetrachloride. On cooling a precipitate formed, which was identified as 3,3′-thenil. The NMR spectrum showed a typical AMX-spectrum at low field. The reaction was repeated using two equivalents of 3-thienyllithium. The yield of 3,3′-thenil was 28 %.

In the same way as above 2-thienyllithium was allowed to react with dimethyl oxalate at −70°. In contrast to the previous experiment the reaction mixture darkened rapidly during the addition of 2-thienyllithium. After work-up a 12 % yield of 2,2′-thenil was isolated.

We have recently observed that 2- or 3-thiophene magnesiumbromide reacts with dimethyl oxalate to give methyl thienyl glyoxalate and methyl dithienyl glycolate.[8] No ketone was formed even at low temperature. The fact that neither glyoxalate nor glycolate was observed in the present experiment indicates that the addition product from equivalent amounts of 3-thienyllithium and dimethyl oxalate is stable under the reaction conditions.

$$3\text{-ThLi} + (\text{COOCH}_3)_2 \longrightarrow$$

$$
\begin{array}{c}
\text{OLi} \\
| \\
3\text{-Th}-\text{C}-\text{COOCH}_3 \\
| \\
\text{OCH}_3
\end{array}
$$

Thus a second equivalent of 3-thienyllithium may attack the ester carbonyl. The resulting product may then give the diketone.

$$
3\text{-ThLi}+3\text{-Th}-\overset{\overset{\text{OLi}}{|}}{\underset{\underset{\text{OCH}_3}{}}{\text{C}}}-\text{COOCH}_3 \longrightarrow
$$

$$
\begin{array}{c}
\text{OLi}\quad\text{OLi} \\
|\qquad| \\
3\text{-Th}-\text{C}----\text{C}-3\text{-Th} \\
|\qquad| \\
\text{OCH}_3\,\text{OCH}_3
\end{array}
$$

$$\longrightarrow 3\text{-Th}-\text{CO}-\text{CO}-3\text{-Th}$$

Although the yield is not high, compared to other methods the reaction between 3-thienyllithium and dimethyl oxalate offers a convenient route to 3,3′-thenil.

Experimental. NMR spectra were obtained with a Varian A 60A Analytical NMR spectrometer at ambient temperature using deuterochloroform as solvent and with tetramethylsilane as internal standard. The shifts are measured in ppm downfield relative to tetramethylsilane. Infrared spectra were recorded with a Perkin Elmer Model 225 Grating Infrared Spectrometer using carbon tetrachloride as solvent. The elemental analyses were carried out at the Department of Analytical Chemistry, University of Lund. All melting-points are uncorrected.

3,3′-Thenil. A solution of 16.3 g (0.1 mole) 3-bromothiophene in 50 ml ether cooled to −70° was added dropwise under nitrogen to 0.1 mole ethyllithium in 140 ml ether at −70°.[7] The resulting 3-thienyllithium solution cooled to −70° was then added dropwise under nitrogen to 5.9 g (0.05 mole) dimethyl oxalate in 150 ml ether at −70°. After stirring for 1 h the cooling bath was removed and when the temperature reached 0° dilute sulfuric acid was added. The ether layer was separated and washed first with dilute sodium bicarbonate solution then with water and finally dried over anhydrous sodium sulphate. After filtration and removal of the solvent, the residue was dissolved in a small amount of carbon tetrachloride. On cooling 2.0 g substance crystallized. The mother liquid was evaporated to dryness and the residue was chromatographed on silica gel. Using benzene as eluent another 1.1 g substance was obtained. Altogether 3.1 g (28 %) was obtained and identified as 3,3′-thenil, M.p. 73.5−75.5° (lit.[6] 75−76°). (Found: C 53.9; H 2.50; S 28.7. Calc. for C$_{10}$H$_6$O$_2$S$_2$: C 54.0; H 2.72; S 28.85).

The IR spectrum showed carbonyl absorption at 1660 cm^{-1}. The NMR spectrum showed signals for three quartets at 7.47, 7.80, and 8.35 ppm. These were assigned as the thiophene ring protons in the 5-position, the 4-position, and 2-position, respectively, ($J_{2,4}=1.4$ cps, $J_{2,5}=3.0$ cps, $J_{4,5}=5.4$ cps).

2,2′-Thenil. 2-Thienyllithium was prepared from 11.3 g (0.135 mole) thiophene in 75 ml ether and 0.135 mole ethyllithium in 130 ml ether according to literature procedure.[9] This solution was then cooled to −70° and added as above to 8.0 g (0.068 mole) dimethyl oxalate in 200 ml ether at −70°. After work-up in the usual manner the dark residue was chromatographed on silica gel. Using benzene as eluent 1.8 g (12 %) of 2,2′-thenil was obtained, m.p. 82−84° (lit. 81−82°,[4] 83−. 84°[3]). (Found: C 53.8; H 2.78; S 28.8. Calc. for C$_{10}$H$_6$O$_2$S$_2$: C 54.0; H 2.72; S 28.85).

The IR spectrum showed carbonyl absorption at 1650 cm⁻¹. The NMR spectrum showed signals for three quartets at 7.25, 7.92, and 8.16 ppm. These were assigned as the thiophene ring protons in the 4-position, the 5-position, and the 3-position, respectively, $(J_{3,4} = 4.0$ cps, $J_{3,5} = 1.2$ cps, $J_{4,5} = 5.2$ cps).

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The Chlorination of Diethyl Sulfide

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Polyhalogenation of sulfides is comparatively little investigated. Truce *et al.*[1] found that when dimethyl sulfide was chlorinated, all three hydrogens at one carbon atom are replaced by chlorine before the second methyl group is chlorinated. Similar results were obtained by Paquette for the chlorination of dibenzyl sulfide and dibenzothiepin; α,α-dichloro derivatives were the main products.[2]

These sulfides contained only α-protons, and no comprehensive investigation seems to have been made for sulfides with α- and

β-protons. Diethyl sulfide is a suitable compound for such an investigation. Bordwell and Pitt obtained, from the chlorination with sulfuryl chloride,[3] a 75 % yield of α-chloroethyl sulfide, but it was found that this compound was much less stable than chloromethyl sulfides, turning dark soon after distillation.[3-5] They also found that all α-chlorosulfides containing β-hydrogens, when formed in heated solution, undergo immediate elimination to α,β-unsaturated sulfides, which in turn react further with the chlorinating agent or polymerize.[3] They also discuss the possibility of contamination by sulfenyl chlorides in the product. With the exception of thiacyclobutane, which yielded γ-chloropropanesulfenyl chloride, no sulfenyl chlorides were detected.[3]

Experiments with diethyl sulfide and two equivalents of sulfuryl chloride in refluxing methylene chloride confirm Bordwell's theories. By NMR and VPC a large number of products were detected. Careful distillation on a Büchi spinning band distillation column yielded low yields of two pure fractions. A lower boiling fraction, b.p. 53°C/14 mm, consisted of approximately a 1:1 mixture of the two *cis-trans* isomers of α,β-dichlorovinyl ethyl sulfide (I). The mass spectrum gave MW = 156 and elementary analyses agree with the empirical formula $C_4H_6Cl_2S$. The IR-spectrum showed a strong band at 1560 cm⁻¹ ($>C=C<$) and the NMR-spectrum contained two overlapping triplets, two overlapping quartets, and two overlapping singlets, ratio 3:2:1. Normant[6] has previously prepared α,β-dichlorovinyl ethyl sulfide, I, (b.p. 56−57/12 mm) which he indicates to be the *trans*-compound but the possibility of geometric isomerism is not discussed.

The higher boiling fraction consisted of the two geometric isomers of 1,2-diethylsulfido-1,2-dichloroethylene (II). Elementary analyses, mass-spectrum, NMR, IR (1515 cm⁻¹), and Raman spectrum (1515 cm⁻¹) are in accordance with this structure. The isolation of these C_6-compounds supports the hypothesis of intermediate sulfenyl chlorides in the reaction.[3]

Diethyl sulfide was also chlorinated by sulfuryl chloride in carbon tetrachloride under nitrogen at −10°C. From the reaction with equivalent amounts of sulfide and sulfuryl chloride was isolated α-chloroethyl sulfide in 50 % yield.

When α-chloroethyl sulfide was chlorinated with one equivalent of sulfuryl