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).

Acknowledgement. The assistance of Mrs. Gun Wallerberg in recording the IR spectra is gratefully acknowledged.

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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]

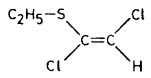
Experiments with diethyl sulfide and two equivalents of sulfuryl chloride in refluxing methylene chloride confirm Bordwell's theories. By NMR and VPC a large number of products were detected. Careful distillation on a Büchi spinning band distillation column yielded low yields of two pure fractions. A 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.

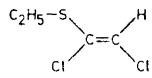
The higher boiling fraction consisted of the two geometric isomers of 1,2-diethylsulfido-1,2-dichloroethylene (II). Elementary analyses, mass-spectrum, NMR, IR (1515 cm^{-1}), and Raman spectrum (1515 cm^{-1}) are in accordance with this structure. The isolation of these C_6-compounds supports the hypothesis 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

chloride under these conditions (−10°C) immediate NMR-analyses of the crude product indicated that the main product





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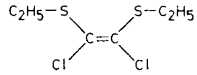

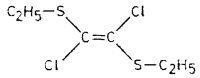

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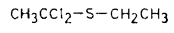

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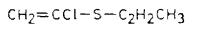

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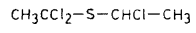

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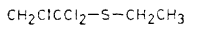

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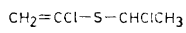

VII

was α,α-dichloroethyl ethyl sulfide (III), and that only minute amounts of unsaturated compounds, *e. g.* α-chlorovinyl ethyl sulfide (IV), were present. The amount of unsaturated sulfide increased after one night in the refrigerator and even more at room temperature. Distillation even under reduced pressure (0.2 mm) yielded a mixture of saturated and unsaturated sulfides.

Diethyl sulfide was chlorinated with 2—8 equivalents of sulfuryl chloride at −10°C in carbon tetrachloride, and the crude products analyzed by NMR. In addition to the mono- and α,α-dichloro sulfide III discussed above, were also observed α,α-dichloroethyl α-chloroethyl sulfide (V) and α,α,β-trichloroethyl ethyl sulfide (VI) together with unidentified higher substituted chlorosulfides and products formed from fission of the sulfide molecule.

The crude product from the reaction with two equivalents of sulfuryl chloride was refluxed in carbon tetrachloride for 3 h followed by distillation on a spinning band column. A 26 % yield of α-chlorovinyl ethyl sulfide (IV) was obtained, b.p. 47°C/30 mm. The NMR-spectrum contained a triplet, a quartet, and a singlet, ratio 3:2:2.

Evaporation of the solvent in the cold from reactions with 3—8 equivalents of sulfuryl chloride gave crude products, which after one week at room temperature contained large amounts of unsaturated sulfides, *e.g.* α-chlorovinyl ethyl sulfide (IV), *cis*- and *trans*-α,β-dichlorovinyl ethyl sulfide (I) and α-chlorovinyl α-chloroethyl sulfide (VII).

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