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INVESTIGATIONS OF DI-THIENYLGLYCOLIC ESTERS

III. REARRANGEMENT OF THE CARBONIUM ION FORMED FROM METHYL 3,3'DI-THIENYLGLYCOLATE.[1]

Börje Östman and Stefan Sjöberg*
Research Institute of National Defence, Dept. 1,
S-172 04 Sundbyberg 4, Sweden.

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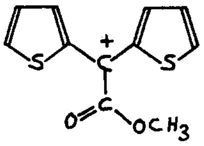
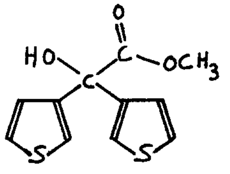
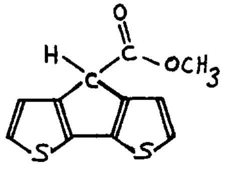
Recently Nilles and Schuetz (2) reported the NMR spectrum of methyl 2,2'di-thienylglycolate dissolved in a mixture of chlorosulfonic acid and methylenedichloride. Consistent with their interpretation of the spectrum as the carbonium ion (I)



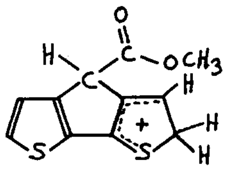
I



II



III



III'

was the fact that the corresponding α-ethoxy glycolate was obtained upon quenching with ethanol (2).

According to the calculated MO energies of the isomeric thenyl carbonium ions (3) the 3-thenyl ion is destabilized with about 2 kcal/mol with respect to the 2-thenyl ion. Hence we decided to repeat the experiment (2) with methyl 3,3'di-thienylglycolate (II) (4) in order to see the effects of the predicted relative destabilization.

The NMR spectrum obtained when II was dissolved in $ClSO_3H/CD_2Cl_2$ mixture is shown in Fig. 1a. When this strongly magenta coloured solution was quenched with methanol or ethanol the product III and some polymeric material was isolated.

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* Present address: Chemical Institute, University of Uppsala, Uppsala, Sweden.

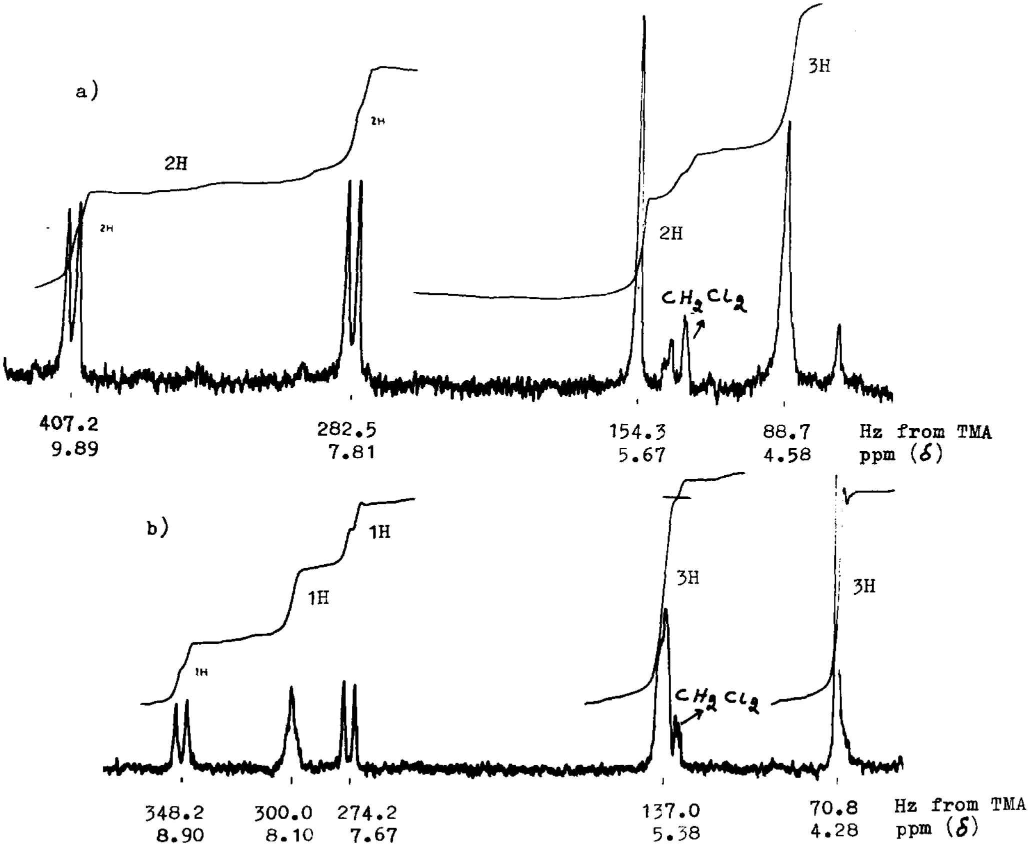


Fig.1. 60 MHz spectrum of a mixture of 1.25×10^{-4} moles of II in 1.34g 25 % (w/w) $ClSO_3H/CD_2Cl_2$ (prepared at -78°C) at a) -55°C (IV) after 110 min. b) -25°C (III') after 80min. Shift positions given in Hz relative $(CH_3)_4N^+$ (TMA) /3.10 ppm from TMS (5)/.

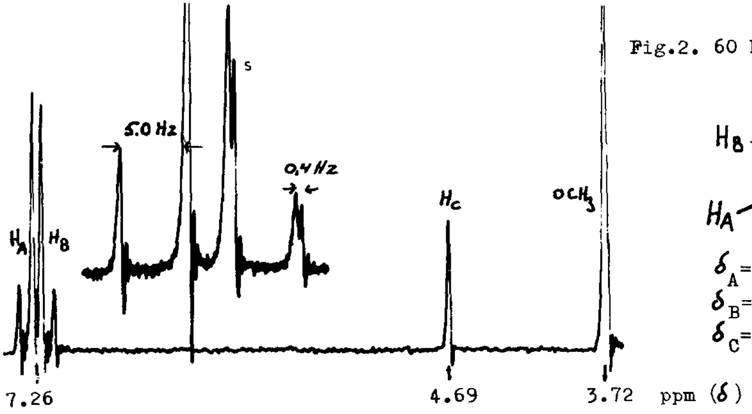
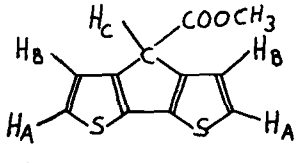


Fig.2. 60 MHz spectrum of III in CH_3CN.



δ_A= 7.33 ppm

δ_B= 7.20 ppm

δ_C= 4.69 ppm

J_{AB}= 5.0 Hz

J_{BC}= 0.4 Hz

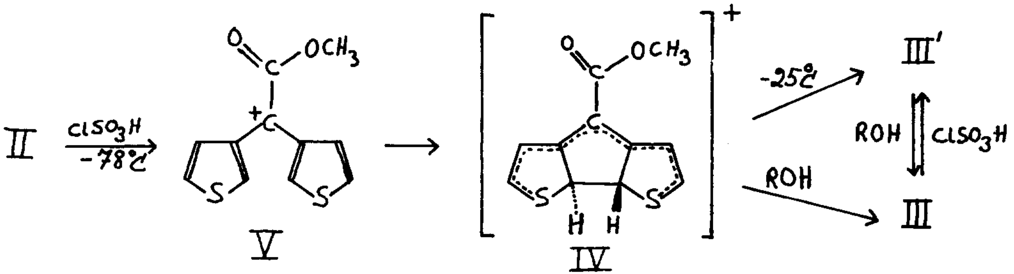
The yield of III was ca. 40%. Its structure was identified with the NMR spectrum (Fig. 2), molecular ion and elemental analyses. The experimental and analytical details will be published separately (6). Spectral data suggest that one of the two main components of the polymeric material is trimeric (6). None of these contained any ether alkoxy groups, however.

If the reaction mixture was allowed to remain in the NMR probe at -25°C, the spectrum of Fig. 1a gradually changed until the spectrum shown in Fig. 1b was recorded. As can be seen from Fig. 1a the change at -55°C is very slow. It should be observed that in the 2,2'dithienyl case the carbonium ion spectrum did not undergo any changes even when the temperature was increased to +30°C (2).

When the mixture represented by the spectrum of Fig. 1b was quenched, the only ether soluble product was III /yield 84 % (6)/.

Finally, it was found that when III was dissolved in $ClSO_3H/CD_2Cl_2$ with an added amount of water (corresponding to the water formed in the reaction of the acid with the hydroxy ester) the NMR spectrum at -25°C was identically the same as the one shown in Fig. 1b. We suggest that Fig. 1b is the spectrum of III', which is in agreement with the following interpretation. The low field doublets /J=5 Hz/ are due to the protons 4 and 5 of the unprotonated ring of III' /J_{45} ~ 5 Hz (7)/, and the unresolved signal in between the two doublets is proton 4 of the protonated ring. The resonance at 137 Hz (δ=5.4 ppm) is due to the methine proton and the two protons of the protonated α-position. The shift of the latter agrees well with the result of Hogeween (8) who found the resonance of the protonated 2-position at 5.22 ppm in the protonation complex of 3-methylthiophene. The high field signal at 70.8 Hz (4.28 ppm) is due to the OCH_3 group.

The following scheme accounts for the formation of III'and III from II.



The intermediate ion IV provides a rationale for the NMR spectrum of Fig. 1a. Thus the two low field doublets (J=5 Hz) are assigned to the two pairs of protons 5 and 4, respectively and the resonance at 154 Hz (5.67 ppm) is assigned to the two angular hydrogens. The OCH_3 protons are found at 88.7 Hz (4.58 ppm). In analogy with the thermal electrocyclization* of the pentadienyl cation system (9), the structure IV would result from the ion V. Due to the conrotatory mode of such cyclizations the angular hydrogens of the ion IV are then predicted to be trans provided the Woodward-Hoffmann rules are applicable also in the present case (9). Owing to the symmetry of cation IV the angular hydrogens are magnetically equivalent, which holds also for the cis arrangement. Thus the steric arrangement of the angular hydrogens is not settled. The possibility of IV to attain coplanarity is conceivably the driving force behind the rearrangement IV → III.* The polyenic character of the reactive ion IV could easily explain the formation of polymers obtained upon ethanol quenching (6).

We conclude that the difference in behavior of the ions I and V is in harmony with the predicted difference in charge localization.

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REFERENCES

1. Part II. A. Meyerhöffer, Acta Cryst., 26, 341 (1970).
2. G.P. Nilles and R.D. Schuetz, Tetrahedron Letters, 1969, 4313.
3. B. Östman, FOA Reports, 3 (1969) 1, J. Am. Chem. Soc., 87, 3163 (1965).
4. Part I. K. Nyberg, B. Östman and G. Wallerberg, Acta Chem. Scand., 24, (1970). In press.
5. N.C. Deno et al., J. Am. Chem. Soc., 85, 2991 (1963).
6. S. Sjöberg, to be published.
7. J.W. Emsley, J. Feeney and L.H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 2, Pergamon Press, Oxford, 1966, p. 802.
8. H. Hogeveen, Rec. Trav. Chim., 85, 1072 (1966).
9. R.B. Woodward and R. Hoffmann, Angew. Chemie, 81, 797 (1969).

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