Within experimental error, the perchlorate oxygen atoms form regular tetrahedra, and the average Cl – O bond distance of 1.47 Å found in the present structure is in agreement with the accepted value of 1.46 Å given by Cruickshank.[5] It is also noted that the two perchlorate positions are related by a rotation of approximately 90° around an axis through the centre of the chlorine atom.

A more detailed examination of intra- and intermolecular bond lengths has to wait until a new data set has been collected from a crystal kept at lower temperature (liquid nitrogen). We believe that this work, which is now in progress will allow a complete refinement of the obtained structure model.

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1. Scheringer, C. *Acta Cryst.* **16** (1963) 546.
2. von Glehn, M., Kierkegaard, P., Norrestam, R., Rönnquist, O. and Werner, P.-E. *Acta Chem. Scand.* **24** (1970) 3701.
3. Leijonmarck, M. and Werner, P.-E. *Acta Chem. Scand.* **24** (1970) 2916.
4. Norrestam, R., Torbjörnsson, L. and Müller, F. *Acta Chem. Scand.* **26** (1972). *In press.*
5. Cruickshank, D. W. J. *J. Chem. Soc.* **1961** 5486.
6. Koenig, D. *Private communication.*

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On a Synthesis of Thieno-annelated Five-membered Heterocyclics

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Recently, a new route to the benzo[b]-thiophene series has been described, consisting of heating cinnamic acids with thionyl chloride and pyridine, which leads to 3-chloro-2-benzo[b]thiophenecarbonyl chlorides.[1-3] The acid chlorides could then in the usual way be transformed to the acids and their derivatives. The disadvantage of this method is that, if the benzene ring contains substituents which activate electrophilic substitution, polychlorination is obtained. Thus, *p*-methoxycinnamic acid yields 3,7-dichloro-6-methoxy - 2 - benzo[b]thiophenecarbonyl chloride in 40 % yield.[3] The reaction is normally slow; six days heating at 100°C was necessary to obtain a 48 % yield with cinnamic acid.[3] Gronowitz and coworkers have for some time been interested in the chemistry and spectroscopic properties of thiophenes annelated to five-membered aromatic heterocyclics. Methods for the synthesis of thieno[2,3-b]thiophene [4] and seleno[2,3-b]thiophene [5] have been described, and the NMR spectra [6,7] and chemical properties [8] of some derivatives studied.

We were therefore interested in investigating the scope of the cinnamic acid ring-closure for the synthesis of thieno-, seleno-, and furothiophenes. A recent paper by Wright [9] on the preparation of 3-chlorothieno[3,2-b]thiophene derivatives from 3-(2-thienyl)acrylic acid has prompted us to publish the results we have hitherto obtained.

Wright found that the reaction mixture obtained from 3-(2-thienyl)acrylic acid, thionyl chloride, and pyridine was rather complex. He isolated 11 – 13 % of 3-chloro - 2 - thieno[3,2-b]thiophenecarbonyl chloride. From the mother liquor, methyl 3,5 - dichloro - 2 - thieno[3,2-b]thiophenecarboxylate and methyl 2-chloro-3-(5-chloro-2-thienyl)acrylate were obtained after reaction with methanol, along with unidentified by-products. When chlorobenzene was used as solvent, 3,5-dichloro-

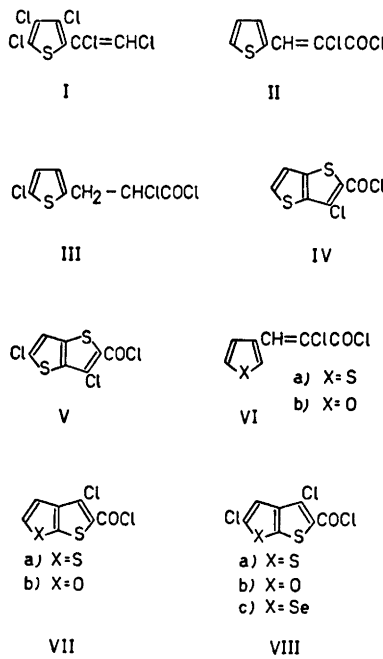
[3,2-b]thiophene-2-carbonyl chloride was isolated in 13 % yield.

We reacted 3-(2-thienyl)-, 3-(3-thienyl)-acrylic acid, 3-(3-furyl)acrylic acid, and 3-(3-selenienyl)acrylic acid with thionyl chloride and pyridine using chlorobenzene as solvent, as these conditions gave the best yields with cinnamic acids. The formation of products was followed directly by combined VPC-MS analysis. This became somewhat complicated due to partial hydrolysis of the acid chlorides, when the mass spectra were recorded.

Structure assignments of the products formed, which in some cases are tentative, are derived from the composition of the molecular ions based on their isotopic clusters and to some extent on the fragmentation patterns.

The mixture obtained upon reaction of 3-(2-thienyl)acrylic acid with thionyl chloride was, as indicated by the results of Wright, rather complex. VPC indicated the formation of at least 12 compounds, of which 5 were formed in minor amounts. The structures and relative area percentages were the following (the compounds are given in the order of increasing retention time): 2-chloro-2-(3,4,5-trichloro-2-thienyl)vinylchloride (I) (3.4 %), 2-chloro-3-(2-thienyl)acrylic acid chloride (II) (11.4 %), 2-chloro-3-(5-chloro-2-thienyl)-propionic acid chloride (III) (9.5 %), 3-chlorothieno[3,2 - b]thiophene-2-carbonyl chloride (IV) (8.7 %), 3,5-dichlorothieno-[3,2-b]-2-carbonyl chloride (V) (30.2 %), two unknown compounds, most probably having the composition $C_7HCl_3OS_3$ (20.5%) and $C_7Cl_4OS_4$ (6.6 %). The five minor components gave a total area percentage of 9.7 %. Attempts to obtain pure compounds by classical separation methods have hitherto been unsuccessful.

We had much greater success in applying the cyclization reaction to 3-(3-thienyl)-acrylic acid. After 24 h of reaction, three main compounds were detected, namely 2-chloro-3-(3-thienyl)acrylic acid (VIa) (4.5 %), 3-chloro-2-thieno[2,3-b]thiophene-carbonyl chloride (VIIa) (79.1 %), and 3,5-dichloro-2-thieno[2,3-b]thiophenecarbonyl chloride (VIIIa) (9.5 %). In addition, six minor peaks were observed in the gas chromatogram, comprising 6.9 area percent. From this mixture, pure 3-chloro-2-thieno-[2,3-b]thiophenecarboxylic acid could be obtained in 62 % yield after hydrolysis, which by dechlorination with copper in propionic acid in almost quantitative yield could be converted to 2-thieno[2,3-b]thiophenecarboxylic acid. As this acid can easily be decarboxylated to thieno[2,3-b]-thiophene by copper and quinoline,[4] this opens an alternative route to this liquid thiophthene. We are continuing experiments in order to find conditions for a one-step dechlorination-decarboxylation.



The corresponding reaction with 3-(3-furyl)acrylic acid was much more complex, as not less than nineteen peaks were observed in the gas chromatogram after 7.5 h reaction time. The five major peaks were the following: 2-chloro-3-(3-furyl)acrylic acid chloride (VIb) (18.2 %), 3-chloro-2-thieno[2,3-b]furancarbonyl chloride (VIIb) (25.5 %), 3,5-dichloro-2-thieno[2,3-b]furan-carbonyl chloride (VIIIb) (8.0 %), and two isomeric compounds (7.1 % and 11.1 %) with the molecular formula $C_7Cl_4O_2S$, which corresponds to completely chlorinated thienofurancarboxylic acid chlorides. The remaining fourteen peaks comprised an area of 30 %.

We have also carried out some experiments with 3-(3-selenienyl)acrylic acid. Also in this case the reaction mixture was rather complex and at least nine peaks were observed in the gas chromatogram. It is, however, somewhat promising as the main component (30 – 40 %) is 3,5-dichlo-

roseleno[3,2-b]thiophenecarboxylic acid chloride (VIIIc). In addition the formation of 2-chloro-3-(2,4,5-trichloro-3-selenienyl)-acrylic acid chloride (14.8 %) appears to be established.

We are continuing our studies on the structure of the other major products formed in the reaction between heterocyclic substituted acrylic acids and thionyl chloride. We also hope that through the use of appropriate dechlorination reactions, this reaction can become of preparative value for the synthesis of thieno-annelated five-membered heterocyclics.

Experimental. General procedure for the reactions of acrylic acids with thionyl chloride. A mixture of 0.10 mol of the acrylic acid, 0.8 ml of anhydrous pyridine, 0.50 mol of thionyl chloride, and 100 ml of freshly distilled chlorobenzene was usually refluxed until the acrylic acid chloride had disappeared. The mixture was analysed directly by VPC using an OV 17 (3 %) on gas chrom Q column. With 3-(3-thienyl)acrylic acid [10] and 3-(3-selenienyl)-acrylic acid the reaction was stopped after 24 h, with 3-(3-furyl)acrylic acid after 7.5 h, and with 3-(3-thienyl)acrylic acid [11] after 96 h.

3-Chlorothieno[2,3-b]thiophenecarboxylic acid. To 22.1 g of crude acid chloride mixture obtained from 13.9 g of 3-(3-thienyl)acrylic acid,[10] 275 ml of dioxane and 44 ml of water were added and the mixture refluxed for 20 h. The mixture was evaporated to dryness and the residue dissolved in hot 96 % ethanol and some insoluble residue filtered off. After evaporation, the residue was recrystallized from 60 % ethanol, yielding 12.5 g (63 %) of the title compound, m.p. 246–248°C. NMR ($(CD_3)_2SO$): $\tau_{4 \text{ or } 5}=2.25$ ppm, $\tau_{5 \text{ or } 4}=2.64$ ppm, $J_{45}=5.3$ Hz. [Found: C 38.2; H 1.36; Cl 16.5; S 30.0. Calc. for $C_7H_3ClO_2S_2$ (218.7): C 38.45; H 1.38; Cl 16.21; S 29.32.]

2-Thieno[2,3-b]thiophenecarboxylic acid. A mixture of 6.0 g of 3-chloro-2-thieno[2,3-b]-thiophenecarboxylic acid and 5.0 g of copper powder in 100 ml of propionic acid was refluxed for 24 h. After cooling, 5 N hydrochloric acid was added, the copper filtered off and the aqueous phases extracted with ether. Evaporation of the ether gave 3.6 g (73 %) of 2-thieno-[2,3-b]thiophenecarboxylic acid with the same physical properties as an authentic sample.[4] An additional 1.4 g was obtained by washing the copper precipitate with acetone.

3-(3-Selenienyl)acrylic acid. A mixture of 16.8 g (0.11 mol) of 3-formylselenophene,[12,13]* 23.0 g (0.22 mol) of malonic acid, 55 ml of anhydrous pyridine and 19 ml of piperidine was heated on a water bath for 2 h, and then heated to boiling for 10 min. After cooling, the solution was poured onto water and acidified with 5 N hydrochloric acid. The precipitate was filtered off and recrystallized from 45 % aqueous ethanol, yielding 16.6 g (75 %) of the title compound, m.p. 147–150°C. NMR ($CDCOCD_3$): $\delta_2=8.47$ ppm (complex multiplet); $\delta_{COOH}=8.87$ ppm; $\delta_5=8.15$ (octet); $\delta_4=7.72$ ppm; $\delta_{CH=}=7.70$ ppm; $\delta_{=CHCOOH}=6.37$ ppm; $J_{CH=CH}=15.6$ Hz, $J_{45}=5.6$ Hz; $J_{24}=1.3$ Hz; $J_{25}=2.4$ Hz; $J_{45=CH}=0.6$ Hz. [Found: C 41.77; H 2.96; Se 39.31. Calc. for $C_7H_6O_2Se$ (201.1): C 41.81; H 3.00; Se 39.26.]

3-(3-Furyl)acrylic acid. This compound was prepared in the same way as described above from 17.9 g (0.22 mol) of 3-furanaldehyde,[14] 46.5 g of malonic acid, 1.12 ml of anhydrous pyridine, and 3.7 ml of piperidine, yielding 24.1 g (89 %) of the title compound, m.p. 145–155°C after recrystallization from 45 % aqueous ethanol. NMR (CD_3COCD_3): $\delta_{COOH}=10.25$ ppm; $\delta_2=7.90$ ppm (complex multiplet); $\delta_{CH=}=7.61$ ppm; $\delta_5=7.57$ ppm (complex multiplet); $\delta_4=6.80$ ppm (complex multiplet); $\delta_{CHCOOH}=6.24$ ppm; $J_{CH=CH}=15.8$ Hz. [Found: C 60.4; H 4.36. Calc. for $C_7H_6O_3$ (138.1): C 60.87; H 4.38].

NMR spectra were recorded on a Varian A-60 NMR spectrometer and mass spectra on an LKB A-9000 mass spectrometer. Analytical VPC was carried out with a Perkin-Elmer 900 gas chromatograph connected with a Varian 480 digital integrator. An OV 17 (3 %) on gas-chrom Q column was used for all analyses. Elemental analyses were carried out at the Analytical Department of the Chemical Institute, University of Lund, and by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr.

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1. Krubsack, A. J. and Higa, T. *Tetrahedron Letters* **1968** 5149.
2. Nakagawa, S., Okumura, J., Sakai, F., Hoshi, H. and Naito, T. *Tetrahedron Letters* **1970** 3719.
3. Wright, Jr., W. B. and Brabander, H. J. *J. Heterocycl. Chem.* **8** (1971) 711.
4. Gronowitz, S. and Persson, B. *Acta Chem. Scand.* **21** (1967) 812.
5. Bugge, A. *Acta Chem. Scand.* **23** (1969) 1823.

* In this laboratory much higher yields than those stated in Ref. 12 have been obtained.

6. Bugge, A., Gestblom, B. and Hartmann, O. *Acta Chem. Scand.* **24** (1970) 105.
7. Bugge, A., Gestblom, B. and Hartmann, O. *Acta Chem. Scand.* **24** (1970) 1953.
8. Bugge, A. *Acta Chem. Scand.* **25** (1971) 27.
9. Wright, Jr., W. B. *J. Heterocycl. Chem.* **9** (1972) 879.
10. Mikailovic, M. L. J. and Tot, M. *J. Org. Chem.* **22** (1957) 652.
11. King, W. J. and Nord, F. F. *J. Org. Chem.* **14** (1949) 405.
12. Paulmier, C. and Pastour, P. *Compt. Rend.* **C 265** (1967) 926.
13. Yur'ev, Yu. K., Magdesieva, N. N. and Monakhova, A. T. *Khim. Geterotsikl. Soedin.* **4** (1968) 645.
14. Gronowitz, S. and Michael, U. *Arkiv Kemi* **32** (1970) 283.

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Lanthanide Induced Chemical Shifts in 5,5-Dimethyl-1,3,2-dioxaphosphorinan-2-ones with Respect to the Conformational Preference of the 2-Substituent

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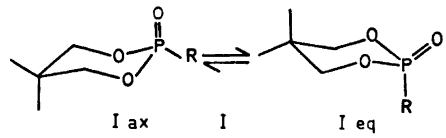
Although exeptions occur,[1,2] the majority of work considering configuration/conformation in substituted or unsubstituted 1,3,2-dioxaphosphorinan-2-ones shows that the geometrical arrangement which gives the thermodynamically most stable molecule, is a chair-like structure, presumably flattened at the phosphorus end of the ring.[2-7] The stereochemistry around the phosphorus atom, that is, whether the 2-substituent is axially or equatorially oriented, is, however, open to question. In cases where crystal structures have been determined, the P=O bond is uniformly oriented equatorially. This need not be the situation in solution. Generally, an equilibrium between two conformers, having the P=O bond axial and equatorial, respectively, should be considered, *i.e.*, for 5,5-dimethyl-1,3,2-dioxaphosphophorinan-2-ones:



I ax I I eq

The potential of lanthanide NMR shift reagents for assignment of protons in complex molecules is now well documented.[8] In principle, these applications are based on the equation:

$$\Delta\nu_i = K(3\cos^2\phi_i - 1)R_i^{-3} \qquad (1)$$

where K is a constant, $\Delta\nu_i$ is the chemical shift induced in proton H_i on complexation of the substrate with the shift reagent, R_i the distance between the proton H_i and the lanthanide in the complex, and ϕ_i the angle between the vector R_i and the principal axis of the complex.

According to eqn. 1, the chemical shifts induced in I on complexation at the phosphoryl-oxygen will depend on the relative contributions from conformers Ia and Ib. Thus there is the possibility of obtaining information with respect to the axial/equatorial preference of the P=O bond in this type of compounds, as proposed by Yee and Bentrude in an article reporting the use of Eu(dpm) for simplifying the NMR spectrum of *trans*-2-methyl-5-*tert*-butyl-1,3,2-dioxaphosphorinan-2-one.[9]

On this background, the derivatives listed in Table 1 have been prepared, and their chemical shifts, ν_i, measured as a function of mol fraction, x, of the shift reagent Eu(fod)$_3$.[10] In all experiments the substrate concentration was kept constant equal to 0.100 M.

The effect of adding Eu(fod)$_3$ to CCl_4 solutions of compounds Ia and Id is illustrated in Fig. 1. As for the other derivatives studied, there is a linear ν/x-dependence in the low concentration range of the shift reagent. The ν/x-slope in this region of x can therefore be taken as a quantitative measure for the changes in chemical shifts caused by complexation with Eu(fod)$_3$. These slopes, the k-values, are listed in Table 1, together with the POCH coupling constants.

It is seen from Table 1 (but more clearly from diagrams) that derivatives Ia–Ic generate qualitatively very similar ν/x-