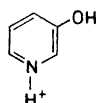




I



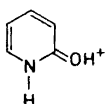
II



III



IV



V

leaving no possibility for a remote attack by a second metal ion. A possible kinetic effect would then be expected to be a retardation due to a decrease of the free energy of the overall reaction.

2-hp exists as the pyridone IV rather than the hydroxy form III.⁵ There is evidence⁶ that in acid solution the oxygen atom is protonated, and that the structure V is present. For this structure there is a possibility of interaction with a metal ion at both the O- and the N-atom, and there is also a conjugated double bond system in the exchange path through the molecule.

k_1 shows a minor increase only with increasing [2-hp], hence k_{-1} also can only show a minor dependence, and the main effect is a strong increase in k_2 . This is also what is observed for the aminopyridines which are present in acid solution in the same forms as V. It is thus plausible to assume that the same mechanism is valid, although more information is needed about the exact composition of the activated complex in the 2-hp catalyzed path.

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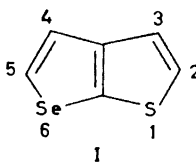
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The Synthesis of Seleno[2,3-b]-thiophene

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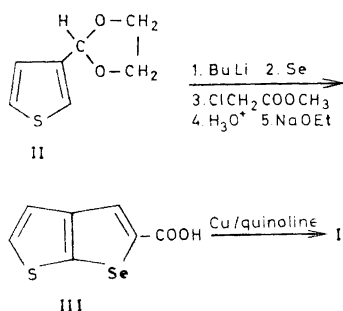
Seleno[3,2-b]thiophene has recently been prepared by Goldfarb *et al.*¹ but the isomeric seleno[2,3-b]thiophene (I) has hitherto not been described. The naming of these new heterocyclic compounds are based on the IUPAC 1957 rules using the thiophene ring as the base component and starting the peripheral numbering with the sulphur atom.



I

In order to obtain the seleno[2,3-b]thiophene, a method similar to the one described by Gronowitz and Persson² for the preparation of thieno[2,3-b]thiophene was adopted. 3-Thiophene aldehyde ethylene acetal (II) was metalated by butyllithium in the 2-position and the resulting thienyllithium compound reacted with selenium according to the method described previously by Goldfarb and Litvinov.³ The intermediate thienylselenolithium derivative was reacted with methyl chloroacetate and hydrolyzed. The methyl(3-formyl-2-thienylseleno)acetate formed was cyclized with alcoholic sodium ethoxide to give the 5-carboxyseleno[2,3-b]thiophene (III). Decarboxylation with copper and quinoline gave seleno[2,3-b]thiophene.

The structure of seleno[2,3-b]thiophene was confirmed by its NMR-spectrum. A discussion of the spectrum will appear elsewhere.



5-Carboxyseleno[2,3-b]thiophene. To a stirred solution of 7.8 g (0.05 mole) 3-thiophenealdehyde ethylene acetal in 50 ml of dry ether in the usual nitrogen-swept Grignard apparatus were added during 10 min at room temperature 55 ml of 1.03 N ethereal butyllithium. The reaction mixture was refluxed for 15 min, then cooled in ice-water, whereafter 4.3 g (0.055 mole) of red amorphous selenium was added in one portion. After stirring for 30 min, the reaction mixture was refluxed for one hour, then cooled in ice-water, before 5.0 g (0.055 mole) of methyl chloroacetate in 20 ml of dry ether was added during 5 min and the solution stirred for 30 min. After standing over-night at room temperature, the reaction mixture was cooled to 0°, 50 ml of ice-cold 2 N hydrochloric acid was added, and the mixture was stirred for one hour. The aqueous phase was extracted once with ether, the combined ethereal solutions were treated with water and saturated sodium bicarbonate solution, then dried over anhydrous magnesium sulphate. The ether solution was added dropwise during 15 min to a solution of 3.5 g (0.15 mole) of sodium in 100 ml of absolute ethanol. The ether was distilled off and the residual ethanolic solution refluxed for 5 h. The alcohol was then distilled off at reduced pressure, the residue was dissolved in water, the resulting solution was extracted with ether and the aqueous phase was acidified with dilute hydrochloric acid leaving 5.3 g (48 %) of 5-carboxyseleno[2,3-b]thiophene. Recrystallisation from water gave m.p. 216° with decomposition.

NMR (acetone): τ_4 1.71; τ_{23} 2.34, 2.56; $J_{23} = 5.5$ cps. The mass spectrum showed a prominent molecular ion at m/e 232 and the relative abundance of the other molecular ions was in agreement with the natural isotope distribution of the elements. (Found: C 36.58; H 1.93. Calc. for $C_7H_4O_2SSe$ (231.1): C 36.37; H 1.74).

Seleno[2,3-b]thiophene. 5.3 g (0.024 mole) of 5-carboxyseleno[2,3-b]thiophene were dissolved in 50 ml of quinoline, 2.4 g of copper bronze was added and the mixture heated with stirring in a nitrogen atmosphere during 3½ h to boiling, 100 ml of quinoline was added dropwise during 3 h to the boiling reaction mixture while a solution of seleno[2,3-b]thiophene in quinoline was allowed to distil off at the same rate as the addition took place. The residual quinoline in the reaction vessel was distilled under reduced pressure, and the combined quinoline phases were cooled with ice, acidified with dilute hydrochloric acid and extracted with ether. The ether was treated with water and with saturated sodium bicarbonate solution and dried above calcium chloride. Evaporation of the ether left 4.0 g of the crude reaction product as an oil. Fractional distillation of this oil gave 2.3 g of the seleno[2,3-b]thiophene b.p.₉ 99–103°. Purification on a preparative gas chromatograph using a 20 % dinonylphthalate on Chromosorb W column gave the compound with m.p. 18.0–20.5°.

NMR (acetone): τ 1.96; τ 2.47; τ 2.53; τ 2.71. $J = 5.8$ cps; $J = 5.3$ cps; $J = 1.1$ cps.

The mass spectrum showed a prominent molecular ion at m/e 188 and the relative abundance of the other molecular ions was in agreement with the natural isotope distribution of the elements.

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