

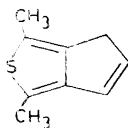
Cyclopenta-thiophenes

II.¹ The Synthesis of 4H-cyclopenta[c]thiophene

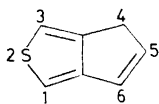
JAN SKRAMSTAD

Division of Organic Chemistry, University of
Lund, Chemical Center, Box 740,
S-220 07 Lund 7, Sweden

A recent publication by Cantrell and Harrison² reporting the synthesis of 1,3-dimethyl-4H-cyclopenta[c]thiophene (I) has prompted the present author to publish this short communication. In connection with work on the tautomeric properties and metallation reactions of cyclopenta-thiophenes now in progress in this laboratory, we were primarily interested in compounds without substituents on the two remaining thiophene carbons. We now wish to report the synthesis of 4H-cyclopenta[c]thiophene (II), the first thiophene analogue of unsubstituted indene to be characterized.



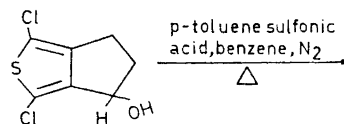
I



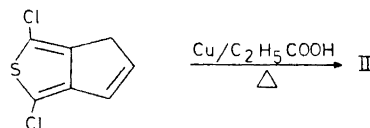
II

The preparation of II was accomplished in two steps from 1,3-dichloro-5,6-dihydro-4H-cyclopenta[c]thiophene-6-ol (III), which was prepared according to MacDowell *et al.*³ Dehydration with *p*-toluene sulfonic acid in refluxing benzene under nitrogen gave 1,3-dichloro-4H-cyclopenta[c]thiophene (IV) in 70–80% yield. The NMR spectrum of IV in CDCl₃ solution consisted of two sharp peaks of equal intensity at $\tau=3.53$ ppm and $\tau=6.88$ ppm. A typical ABX₂ spectrum appeared, however, when (CD₃)₂CO was used as solvent. A: $\tau_{H_6}=3.37$ ppm; B: $\tau_{H_5}=3.47$ ppm; X₂: $\tau_{CH_2}=6.81$ ppm. $J_{AB}=5.7$ c/s, $J_{AX}\sim J_{BX}=1.8$ c/s. The mass spectrum was also in accordance with the proposed structure (see the experimental section).

It was found that IV could be dechlorinated by copper powder in refluxing propanoic acid to give II in 60–70%



III

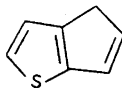


IV

yield after a reaction time of 30 h. The NMR spectrum of II recorded in (CD₃)₂CO solution revealed the structure. The chemical shifts and coupling constants for the hydrogens in the carbocyclic ring were approximately the same as the corresponding data for the dichloro compound (IV), whereas two new bands appeared in the aromatic region due to one hydrogen each. A doublet at $\tau=3.10$ ppm with $J=2.2$ c/s is assigned to the 1-hydrogen and a multiplet centered at $\tau=2.98$ ppm is assigned to the 3-hydrogen. The multiplet consisted of a doublet of triplets ($J=2.2$ c/s and $J=1.4$ c/s, respectively), with a final splitting into doublets ($J=0.7$ c/s). The larger coupling constants is obviously due to coupling between the two aromatic hydrogens (1 and 3). It is noteworthy that this coupling is considerable smaller than the usual 2,5-coupling in open thiophene derivatives (3.20–3.65 c/s),⁴ but is of the same order of magnitude as that found in 5,6-dihydro-4H-cyclopenta[c]thiophene-6-one (2.5 c/s).³ The reason for ascribing the multiplet at $\tau=2.98$ ppm to the 3-hydrogen is that the splitting into a triplet (coupling to the methylene hydrogens) shows a coupling constant comparable with the coupling between the methyl hydrogens and the 2-hydrogen in 3-methylthiophene.⁵ Finally, the doublet of 0.7 c/s is interpretable as a long-range coupling from the 3-hydrogen to the 6-hydrogen (the same splitting is found in the absorptions of the latter). The theory of the straightest zig-zag path⁶ leads to the same assignment. The mass spectrum confirmed the proposed structure (See the experimental section).

It is interesting to note that less than 10 % conversion of IV to II could be achieved when the reaction was carried out in a nitrogen atmosphere, even at much longer reaction times. It is therefore tempting to suggest that oxygen plays a part in this dechlorination reaction.

The fact that II survives more than 30 h in refluxing propanoic acid speaks for its stability. This is in striking contrast to the lack of stability of 4H-cyclopenta[b]thiophene (V), which so far has not been characterized and is only mentioned in the literature as a very unstable compound which rapidly deteriorates.⁷ Even 5-methyl-4H-cyclopenta[b]thiophene (and its tautomer) is very sensitive towards air and acids.⁸ The enhanced stability of II over its b-annulated analogues may be explained in terms of the difference in angle strain in these compounds. The geometry of thiophene⁹ suggests less strain when the carbocyclic ring is fused between the 3- and



V

4-positions. Another point of importance may be that the carbocyclic ring in II formally has the appearance of a cyclopentene ring, whereas in V it may be regarded as a cyclopentadiene ring. It is also worth mentioning that this difference in stability may be looked upon as a Mills-Nixon effect.¹⁰

These questions will, however, be treated in more detail in the forthcoming full paper, where also metallation reactions are to be described.

Experimental. 1,3-Dichloro-4H-cyclopenta[c]thiophene (IV). 3.0 g (0.014 mole) of 1,3-dichloro-5,6-dihydro-4H-cyclopenta[c]thiophene-6-ol³ was dissolved in 200 ml of dry benzene, 0.5 g of *p*-toluene sulfonic acid was added and the solution refluxed under nitrogen for 2 h. The water of reaction was collected in a Dean and Stark water separator. After cooling, the dark red solution was washed twice with water, dried (MgSO₄) and evaporated under reduced pressure. The residue was taken up in pentane (*p.a.*) and rapidly eluted through a short column of acidic alumina. The eluate on evaporation yielded

2.3 g (80 %) of a colourless liquid (without OH-absorption in IR). After distillation, b.p. 70°/2 mm Hg, the purity was better than 99 % according to VPC. The NMR spectrum is given in the theoretical part above. The mass spectrum was in agreement with the proposed structure (M=191.1) showing a typical pattern for the molecular ion caused by the presence of two chlorine atoms (*m/e*, %: 190, 22; 191, 4.1; 192, 15; 193, 1.5; 194, 2.8; 195, 0.3). The dominant fragmentation involved loss of one chlorine giving the base peak (155, 100 %; 156, 9.7; 157, 32; 158, 2.9). The UV spectrum, recorded in 95 % ethanol, gave maxima at 266 m μ (ϵ =10 400) and 232 m μ (ϵ =12 000).

4H-Cyclopenta[c]thiophene (II). 1.7 g (0.009 mole) of 1,3-dichloro-4H-cyclopenta[c]thiophene was dissolved in 25 ml of propanoic acid and 2.0 g of copper powder (electrolytic, Merck) was added. The mixture was refluxed for 30 h. After cooling, the dark green solution was poured into water, the resulting mixture was extracted carefully with ether and the ether extracts washed with sodium bicarbonate solution and water until neutral. After drying (MgSO₄), the ether was evaporated under reduced pressure and the residue taken up in pentane (*p.a.*) and chromatographed as above. This gave 0.7 g (64 %) of a colourless, mobile liquid after evaporation of the pentane. Distillation, b.p. 40°/2 mm Hg, afforded the title compound with a purity of 95 % (VPC), 5 % of the two monochloro compounds also being present (identified by the combined gas chromatograph/mass spectrometer). The mass spectrum confirmed the structure of the title compound. The base peak had a *m/e* value of 122 corresponding to the molecular ion of II. Besides a fragment at *m/e*=121 (95 %), the cracking pattern appeared complex. No fragment containing chlorine could be detected. The UV spectrum recorded in 95 % ethanol gave λ_{\max} =251.5 m μ (ϵ =10 200). The NMR is described above in the theoretical part.

The NMR spectra were recorded on a Varian A 60 spectrometer (with TMS as internal standard). The mass spectra were obtained with an LKB 9000 instrument at an ionization energy of 70 eV. The gas chromatographic inlet system was used with a 3 m SE 30 (1 %) column. VPC analyses were carried out with a Perkin Elmer 900 gas chromatograph using an Apiezon column. The UV spectra were recorded on a Unicam SP 800.

Acknowledgements. For all the facilities kindly placed at my disposal, I express my gratitude to Professor Salo Gronowitz. Technical assistance was given by Mr. Torbjörn Frejd (preparation of some of the intermediates), Mr.

Jan Glans (NMR) and Mrs. Gun-Britt Lindahl (MS). This work has been supported by a grant (rekrueringsstipendium) from *The Norwegian Research Council for Science and Humanities* which, together with financial support from *The Faculty of Science of the University of Lund*, is gratefully acknowledged.

1. Skramstad, J. *Acta Chem. Scand.* **22** (1968) 2445; Paper I.
2. Cantrell, T. S. and Harrison, B. L. *Tetrahedron Letters* **45** (1967) 4477.
3. MacDowell, D. W. H., Patrick, T. B., Frame, B. K. and Ellison, D. L. *J. Org. Chem.* **32** (1967) 1226.
4. Gronowitz, S. *Advan. Heterocyclic Chem.* **1** (1963) 8.
5. Gronowitz, S. *Advan. Heterocyclic Chem.* **1** (1963) 11.
6. Banwell, C. N. and Sheppard, N. *Discussions Faraday Soc.* **34** (1962) 115.
7. Sam, J. and Thompson, A. C. *J. Pharm. Sci.* **52** (1963) 898.
8. Meth-Cohn, O. and Gronowitz, S. *Acta Chem. Scand.* **20** (1966) 1733.
9. Bak, B., Christensen, D., Hansen-Nygaard, L. and Rastrup-Andersen, J. *J. Mol. Spectry.* **7** (1961) 58.
10. Mills, W. H. and Nixon, I. G. *J. Chem. Soc.* **1930** 2510.

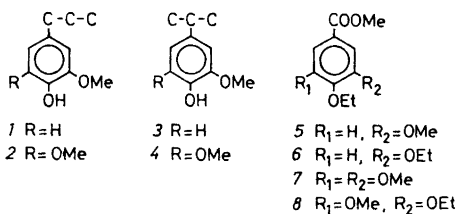
Received February 8, 1969.

Catechol Moieties in Enzymatically Liberated Lignin

T. KENT KIRK and ERICH ADLER

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, Fack, S-402 20 Göteborg 5, Sweden

The methoxyl content of lignin in wood decreases markedly during removal of carbohydrates by certain Basidiomycetes known as "brown-rot" fungi.¹⁻³ Little specifically is known, however, about the effects of these fungi on the lignin;³ the structures of the methoxyl-deficient units in the lignin apparently have not been studied. We have examined such lignin, which is known as "enzymatically liberated lignin",⁴ for the possible occurrence of catechol (*o*-diphenol) moieties, which could arise *via* a net demethylation of guaiacylpropane (1) and syringylpropane (2) units as well as of the corresponding 2-arylpropane structures (3, 4) present^{5,6} in lesser



Correction to "The Determination of Cytochrome *c* Reductase Activity"

SVEN PALÉUS, BRUNO TOTA,
ESKIL HULTIN and
GISELA LILJEQVIST

Biochemical Department, Nobel Medical Institute, Karolinska Institutet, S-104 01 Stockholm, Sweden

The cyanide concentration, as given on p. 4, line 26 from above, is erroneous. The concentration actually used was 7×10^{-3} mM.

Received March 25, 1969.

* *Acta Chem. Scand.* **23** (1969) 1.

amounts in lignin. We used an approach suggested by the work of Hayashi and Namura,⁷ who reported that permanganate oxidation of an ethylated liginosulfonate yielded, among other products, small amounts of 3,4-diethoxybenzoic acid, which must have been derived from catechol units present in the liginosulfonate. The detailed method that we used in the present study was adapted from a technique developed recently in this laboratory in connection with the oxidative degradation of methylated lignins.⁸⁻¹⁰

The enzymatically liberated lignin had been prepared from sapwood of sweetgum (*Liquidambar styraciflua* L.) by the use of *Lenzites trabea* Pers. ex Fries in an earlier study.¹¹ The whole lignin had been separated by preparative gel chromatography