

## Cyclopenta-thiophenes

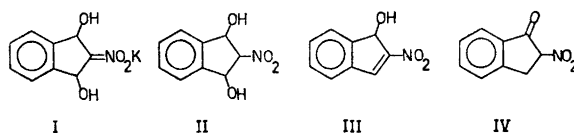
III.<sup>1</sup> Cyclopenta[b]thiophenes from the Reaction Between  
2,3-Diformylthiophene and Nitromethane

JAN SKRAMSTAD

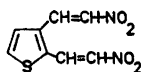
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Contrary to an earlier reported attempt it is shown that 2,3-diformylthiophene gives dihydro-cyclopenta[b]thiophenes in high yields on reaction with nitromethane. A convenient route to one of the two possible thiophene analogues of indane-2-one is thereby opened. The NMR spectra of these new bicyclic compounds are discussed, together with some mechanistic points concerning their synthesis.

The reaction between phthalaldehyde and nitromethane in methanol with potassium hydroxide as base furnishes in high yield potassium-1,3-dihydroxyindane-2-nitronate (I).<sup>2</sup> This compound has been converted to the parent nitro compound (II),<sup>2</sup> to the hydroxy olefin (III)<sup>2,3</sup> and *via* the latter to the keto-tautomer (IV)<sup>4</sup> as well as to 2-nitroindene.<sup>5</sup>



As cyclopenta-thiophenes are of current interest in this Laboratory, the present author thought it worth-while to try to obtain this system by condensing nitromethane with a diformylthiophene, as described for phthalaldehyde. A literature survey disclosed only one attempt in this direction. Adopting the experimental conditions used in the benzene series, Patrick<sup>6</sup> reacted 2,3-diformylthiophene with an excess of nitromethane and potassium hydroxide. However, the product isolated after acidification was not the expected cyclopenta[b]thiophene, but rather 2,3-bis( $\omega$ -nitrovinyl)-thiophene (V). Patrick made no comment on his failure to obtain the cyclized product.

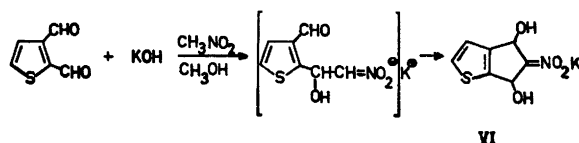


Y

To achieve this, an obvious modification would be to use an equivalent amount of nitromethane and to keep its concentration low during the reaction. This expectation was indeed born out by experiments!

The synthesis of 2,3-diformylthiophene was carried out according to the method of Pastour *et al.*<sup>7</sup> by reacting the ethylene acetal of 3-formylthiophene with butyllithium and *N,N*-dimethylformamide. Subsequent acid hydrolyses gave the diformyl compound. This method was found superior as to yield and purity of product, compared to the other reported method<sup>8</sup> where the formyl groups are introduced by reacting 2,3-dilithiothiophene with *N,N*-dimethylformamide followed by hydrolyses.

2,3-Diformylthiophene was dissolved in methanolic potassium hydroxide at 0–5°, and an equivalent amount of nitromethane was added dropwise. This gave an almost quantitative yield of potassium-5,6-dihydro-4,6-dihydroxy-



VI

4H-cyclopenta[b]thiophene-5-nitronate (VI). The first step in this reaction is probably a condensation of nitromethane with one of the aldehyde groups producing an intermediate potassium-nitronate. Depending on the concentration of nitromethane, the further reaction is either a ring closure to give VI

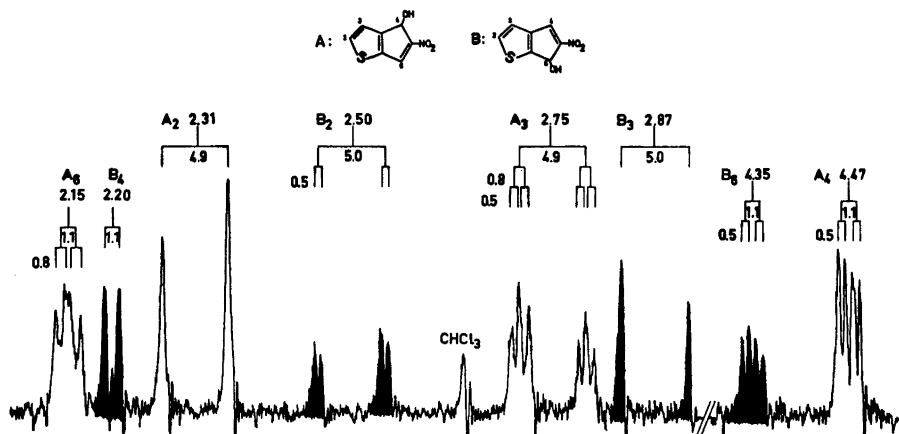
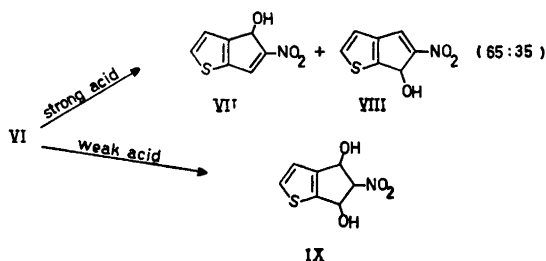


Fig. 1. The NMR spectrum (in  $\text{CDCl}_3$  solution) of a mixture consisting of 65 % of 4-hydroxy-5-nitro-4H-cyclopenta[b]thiophene (VII=A) and 35 % of 6-hydroxy-5-nitro-6H-cyclopenta[b]thiophene (VIII=B). The chemical shifts are given as  $\tau$  values, and the coupling constants are in c/s.

or a condensation with another molecule of nitromethane to give the bis potassium-nitronate. The latter is converted to VI by the action of acid.

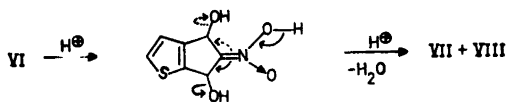
Like the benzene analogue, the nitronate, VI, was easily dehydroxylated when treated with aqueous mineral acid in the cold. The product was (NMR, Fig. 1) a mixture consisting of 65 % of 4-hydroxy-5-nitro-4H-cyclopenta[b]thiophene (VII) and 35 % of 6-hydroxy-5-nitro-6H-cyclopenta[b]thiophene (VIII)



(VIII). When the salt, VI, was treated with a buffered aqueous solution at pH 5 (acetic acid/sodium acetate), the nitro diol, IX, was produced in high yield.

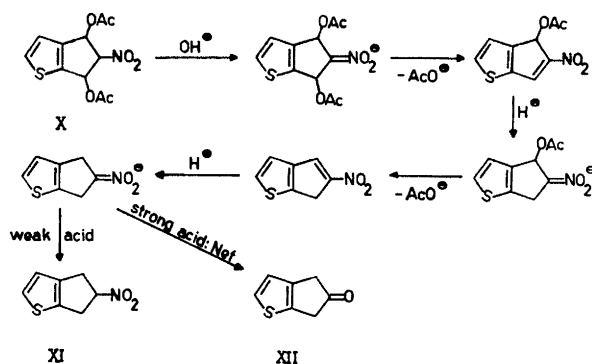
An interesting property of this diol is that it undergoes dehydration only under forcing conditions. Concentrated or dilute mineral acids in the cold have no effect. Refluxing in 10 % hydrochloric acid under nitrogen causes some decomposition. Refluxing in benzene under nitrogen with *p*-toluene sulfonic acid does, however, result in a mixture of the dehydrated compounds VII and VIII.

This great difference in the ease of elimination of hydroxide from the nitronate ion, compared with the loss of water from its parent nitro compound, strongly suggests that the latter is not an intermediate in the dehydroxylation of the former. (The opposite was claimed without proof by Baer *et al.* for the analogous reaction in the benzene series.<sup>2,9</sup>) The probable mechanism involves protonation of the nitronate, VI, to give the nitronic acid. By the action of strong acids this intermediate eliminates water and gives the mixture VII+VIII before any tautomerization to the nitro diol can occur. With weak acids, on the other hand, such tautomerism accounts for the formation of IX.

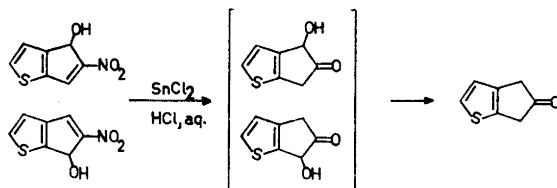


The diol, IX, was converted in high yield to the corresponding diacetate, X, by reaction with acetic anhydride and a trace of sulfuric acid. The diacetate went into solution when added in small portions to an aqueous solution of sodium borohydride with ice-cooling and rapid stirring. After acidification with acetic acid, a white solid could be isolated. The structure was determined

(see NMR Discussion and Experimental) to be 5,6-dihydro-5-nitro-4H-cyclopenta[b]thiophene (XI). When the clear reaction solution was instead poured onto concentrated hydrochloric acid at  $-15^{\circ}$  in order to bring about a Nef reaction,<sup>11</sup> a crystalline solid was isolated. This compound was shown (NMR, MS, IR) to be one of the two thiophene analogues of indane-2-one, *e.g.* 5,6-dihydro-4H-cyclopenta[b]thiophene-5-one (XII). The sequence of steps thought to be involved in these transformations are outlined in the scheme below. The first step is an elimination of acetic acid to produce an  $\alpha,\beta$ -unsaturated nitro compound. It is well documented<sup>5,10</sup> that sodium borohydride is capable of adding hydride ion to conjugated nitro olefins and thereby form nitronates. From the nitronate formed here, a new elimination of acetate takes place, followed by a second reduction step. The resulting nitronate is converted to XI by the action of weak acid or by strong acid to the ketone, XII. Thus, the following reaction sequence is carried out in a single operation: elimination-reduction-elimination-reduction-tautomerization or Nef reaction!



As the ketone, XII, is of great interest in other connections, shorter synthetic pathways were investigated. Indane-2-one has been prepared by reduction of 2-nitroindene with zinc and acetic acid, followed by hydrolyses of the resulting oxime.<sup>12</sup> 2-Nitroindene in turn has been made from III by the action of sodium borohydride in ethanol, followed by acid catalyzed dehydration.<sup>5</sup> Consequently, the mixture of nitro olefins, VII and VIII, was treated with sodium borohydride in ethanol. However, no well-defined product could be isolated after the addition of hydrochloric acid. This failure could have been due to the instability of VII and VIII in the basic reaction medium. Therefore, an acidic reduction path was designed as shown below. It is known



that stannous chloride in hydrochloric acid reduces  $\alpha,\beta$ -unsaturated nitro compounds to oximes,<sup>13</sup> which in acidic medium hydrolyse to ketones.<sup>14</sup> It was hoped that the ketols obtained in this way would undergo a further reduction to the desired ketone by the action of stannous chloride. Stannous chloride reductions of ketols have been described.<sup>15</sup>

When the mixture VII+VIII was reduced by the action of stannous chloride in aqueous hydrochloric acid at  $-10^\circ$ , the ketone XII could be isolated in about 40 % yield! This positive result suggested that a direct conversion of the nitronate, VI, to the ketone was possible. Accordingly, VI was treated in the same way as the mixture VII+VIII, and after work-up, the ketone was isolated in about 50 % yield. One has good reason to believe that the first step in this last reaction is the formation of the usual mixture of VII and VIII, which then undergoes the same reactions as above.

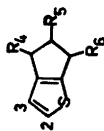
An interesting question concerning this thiophene analogue of indane-2-one is to what degree it shows enolic properties. Indane-2-one itself exists in the solid state and in solution as a ketone.<sup>16</sup> Without fully answering the question at this time, it is safe to say that XII shows very little indication of the enol form in the solid state or in solution as judged from its IR spectra. Just as indane-2-one, the IR spectrum of XII shows two carbonyl bands in carbon tetrachloride solution. Different explanations have been offered for this, including Fermi resonance effects.<sup>16</sup>

The chemistry of XII will be the subject of a future paper.

#### DISCUSSION OF THE NMR SPECTRA

It is evident from Table 1 that dihydro-cyclopenta[b]thiophenes are 2,3-disubstituted thiophenes, giving rise to the characteristic coupling constant of about 5 c/s between the remaining aromatic hydrogens<sup>17</sup> (here  $J_{23}$ ). In these dihydro compounds, the low-field doublet is assigned to the 2-hydrogen in every case. This follows from a comparison with the reported spectra of the unsubstituted 5,6-dihydro-4H-cyclopenta[b]thiophene<sup>6,18</sup> and with the corresponding 6-hydroxy-compound<sup>6</sup> (Table 1). Simple additivity rules<sup>19</sup> support this assignment. Having thus identified the low-field doublets, one notices from the table that these bands show additional splitting, obviously due to long-range coupling into the carbocyclic ring. Inspection of the spectra reveals that the coupling goes to the benzyl-like hydrogens (4 or 6) at the lowest field. The 6-hydrogens, with their proximity to the sulfur atom, have been given this assignment. Thus, the long-range coupling is a 2,6-coupling, and hence of the *para*-benzylic type.<sup>20</sup> Even some small couplings to the other benzyl-hydrogens (the 4-hydrogens) are detectable in the spectra (possibly  $J_{34}$ , that is, of the *ortho*-benzylic type). The magnitude of about 1 c/s of  $J_{26}$  is appreciably larger than the corresponding  $J_{\text{CH}_3-5}$  in 2-methylthiophenes which is  $< 0.4$  c/s.<sup>17</sup> Conformational effects may be responsible for this.

With regard to the stereochemistry of compounds IX and X, one observes that the coupling constants  $J_{45}$  and  $J_{56}$  are identical. This points to the same spatial arrangement of the 4- and 6-hydrogens relative to the 5-hydrogen. The same conclusion was drawn in the benzene case.<sup>2</sup> However, it is difficult

Table I. Chemical shifts ( $\alpha$  values) and coupling constants (c/s) of some 5,6-dihydro-4H-cyclopenta[b]thiophenes.

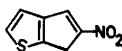
Com- pound	Solvent	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>	H <sub>d</sub>	H <sub>e</sub>	H <sub>f</sub>	J <sub>23</sub>	J <sub>26</sub>	J <sub>45</sub>	J <sub>56</sub>
IX	(CD <sub>3</sub> ) <sub>2</sub> CO	OH	NO <sub>2</sub>	OH	2.46(dd)	3.04(d)	4.60(d)	4.86(t)	4.40(d)	OH variable	5.0	0.8	4.9	4.9
X	CDCl <sub>3</sub>	OAc	NO <sub>2</sub>	OAc	2.53(dd)	3.05(d)	3.70(d)	4.54(t)	3.70(d)	7.85(s)(CH <sub>3</sub> )	5.0	0.8	3.6	3.6
XI	CDCl <sub>3</sub>	H	NO <sub>2</sub>	H	2.80(dt)	3.22(d)	6.55(t)	4.52(tt)	6.55(t)		4.9	1.0	5.5	5.5 ( <i>trans</i> ) 7.0 ( <i>cis</i> )
XII	CDCl <sub>3</sub>	H	= O	H	2.78(dt)	3.08(d)	6.62(bs)	—	6.49(bs)		5.0	1.1		
Ref. 18.	CCl <sub>4</sub>	H	H	H	3.05(d <sup>†</sup> )	3.36(d)					5.0			
Ref. 6	CCl <sub>4</sub>	H	H	H	2.95(dt)	3.28(d)					5.0			
Ref. 6	CDCl <sub>3</sub>	H	H	OH	2.70(d)	3.21(d)					5.0			

s = singlet, d = doublet, t = triplet, bs = broad singlet, dd = doublet with additional doublet splitting, dt = doublet with triplet splitting, tt = triplet with triplet splitting.

to decide whether this is *cis* or *trans* coupling. It is known that  $J_{12}$  (*cis*) and  $J_{12}$  (*trans*) in 1,2-disubstituted indanes are very much influenced by substituents and that it is difficult *a priori* to tell which is the larger.<sup>21</sup> However, in a very recent paper, Angyal and Luttrell<sup>27</sup> claim that protonation of a nitronate, where the nitronate group is flanked by hydroxyl groups, is a thermodynamic controlled process, and that the *trans,trans*-nitrodiol preponderates. Therefore one would expect that IX (and hence X) has the *trans,trans*-configuration.

The NMR spectrum of the mixture resulting from dehydroxylation of VI is recorded in Fig. 1. The bands assigned to VII are denoted A, and the bands assigned to VIII are denoted B, with the latter ones made black to facilitate identification. The assignments regarding the former are as follows: The aromatic hydrogens 2 and 3 absorb at  $\tau = 2.31$  ppm and  $\tau = 2.75$  ppm, respectively, with a mutual coupling constant of 4.9 c/s. The 3-hydrogen shows two long-range couplings. The larger one of 0.8 c/s follows the straightest zig-zag path to the 6-hydrogen. Similar couplings across five bonds in a planar arrangement are well documented in the literature.<sup>1,20,22</sup> The smaller one of 0.5 c/s goes to the 4-hydrogen at  $\tau = 4.47$  ppm and is of the *ortho*-benzylic type. The 4-hydrogen shows the expected allylic coupling to the 6-hydrogen at  $\tau = 2.15$  ppm, the constant being 1.1 c/s.

As to the assignments of the hydrogens in VIII (the B-bands), one problem arises: which of the aromatic hydrogens absorbs at the lowest field? If we make a comparison with 3-( $\omega$ -nitrovinyl)thiophene<sup>23</sup> (where the 5-hydrogen absorbs at a lower field than the 4-hydrogen in spite of the electron withdrawing properties of the nitrovinyl group), we would assign the band at  $\tau = 2.50$  ppm to the 2-hydrogen, and the band at  $\tau = 2.87$  ppm to the 3-hydrogen. This assignment is fully supported by comparison with the NMR spectrum of the closely related compound XIII.<sup>24</sup> Here, the 2-hydrogen signal lies at  $\tau = 2.62$  ppm, and the 3-hydrogen signal at  $\tau = 2.86$  ppm.



XIII

Returning now to Fig. 1, we find that  $J_{23}$  in VIII has the expected value, e.g. 5.0 c/s. The low-field doublet which we have just denoted B<sub>2</sub>, shows additional doublet splitting with a coupling constant of 0.5 c/s. The same splitting is found in the B<sub>6</sub>-band at  $\tau = 4.35$  ppm, which means that this is a 2,6-coupling. It is interesting to note that the same type of coupling was observed in the dihydro-cyclopenta[b]thiophenes found in Table 1. The chemical shifts and coupling constants of the carbocyclic ring in VIII have the values expected.

#### EXPERIMENTAL

*Potassium-5,6-dihydro-4,6-dihydroxy-4H-cyclopenta[b]thiophene-5-nitronate* (VI). An ice-cold solution of 5 g potassium hydroxide in 50 ml of methanol was added to a stirred solution of 5.0 g (0.036 mol) of 2,3-diformylthiophene<sup>7</sup> in 150 ml of methanol kept at

0–5°. Nitromethane, 2.3 g (0.038 mol), in 50 ml of methanol was added slowly with rapid stirring. A white solid soon began to separate. After the addition was complete (30 min), the stirring was continued for another half an hour, and then the solid was collected by filtration by suction. After washing with a little cold methanol, the solid was dried in a vacuum desiccator. The dried product weighed 8.2 g (96 %). The IR spectrum (KBr) showed broad hydroxyl absorptions in the 3500–2500  $\text{cm}^{-1}$  region, no carbonyl absorptions, but a very strong band at 1595  $\text{cm}^{-1}$  attributable to the C=N stretching vibration.<sup>25,26</sup> The spectrum was quite similar to that of the corresponding benzene analogue (produced according to Ref. 2). Also the behaviour on heating was similar; discoloration started at about 150°, and complete charring occurred at about 200°. The product was used directly in the following steps without further purification.

*4-Hydroxy-5-nitro-4H-cyclopenta[b]thiophene (VII) and 6-hydroxy-5-nitro-6H-cyclopenta[b]thiophene (VIII)*. The nitronate, VI, 5.0 g (0.021 mol), was added with rapid stirring to 50 ml of 6 N hydrochloric acid, cooled to –10°. The white solid went into solution, producing a yellow colour. After a few minutes, a yellow solid precipitated. This solid was rapidly filtered, washed with water, and then dried in a desiccator. The yield of crude product was 3.2 g (84 %), m.p. ~115° (dec.). One crystallization from chloroform/hexane gave yellow-brown crystals, m.p. 115° (dec.), with the same NMR spectrum as the crude product. This spectrum revealed the existence of two components in the reaction product, namely the title compounds VII and VIII in the proportion 65:35 (Fig. 1). MS (*m/e*, %): 183, 22 % ( $\text{M}^{\oplus}$ ); 137, 100 %; 136, 100 %. [Found: C 46.0; H 2.95; N 7.45; S 17.7. Calc. for  $\text{C}_7\text{H}_7\text{NO}_2\text{S}$  (183.2): C 45.89; H 2.75; N 7.65; S 17.51.]

*5,6-Dihydro-4,6-dihydroxy-5-nitro-4H-cyclopenta[b]thiophene (IX)*. To a buffered aqueous solution at pH 5 (sodium acetate/acetic acid) was added 8.0 g (0.034 mol) of the potassium salt, VI, with rapid stirring. When most of the white powder had dissolved, the solution was extracted several times with ether. The ether extract was dried ( $\text{MgSO}_4$ ) and the ether evaporated. An almost colourless residue weighing 5.7 g (85 %) was left. One crystallization from ethanol/chloroform gave colourless prisms, melting with decomposition at 150–155°. NMR, see Table 1. IR (KBr): broad band in the 3600–2500  $\text{cm}^{-1}$  region (OH), 1550 and 1370  $\text{cm}^{-1}$  ( $\text{NO}_2$ ). MS (*m/e*, %): 201, 8 % ( $\text{M}^{\oplus}$ ); 154, 100 %. [Found: C 41.9; H 3.60; N 6.95; S 16.5. Calc. for  $\text{C}_7\text{H}_7\text{NO}_4\text{S}$  (201.2): C 41.78; H 3.51; N 6.96; S 15.94.]

*4,6-Diacetoxy-5,6-dihydro-5-nitro-4H-cyclopenta[b]thiophene (X)*. The diol, IX, 5.0 g (0.025 mol), was added to 20 ml of acetic anhydride, cooled in an ice-bath. 5 ml of acetic anhydride, containing a few drops of concentrated sulfuric acid, was added with stirring, causing the solid to dissolve. After half an hour at room temperature, the solution was poured onto ice-water with vigorous stirring. A white solid was collected by filtration, washed with water, and dried in a desiccator. The yield was 6.6 g (93 %) of fine-crystalline material, melting with decomposition at 85–90°. One crystallization from chloroform/petroleum ether gave faint yellow, hard prisms, m.p. 89–91° (dec.). NMR, see Table 1. IR (KBr): C=O stretching at 1760 and 1740  $\text{cm}^{-1}$ , and  $\text{NO}_2$ -bands at 1565 and 1375  $\text{cm}^{-1}$ . MS (*m/e*, %): 285, <1 % ( $\text{M}^{\oplus}$ ); 136, 100 %. [Found: C 46.6; H 3.96; N 5.00; S 11.3. Calc. for  $\text{C}_{11}\text{H}_{11}\text{NO}_6\text{S}$  (285.3): C 46.31; H 3.89; N 4.91; S 11.24.]

*5,6-Dihydro-5-nitro-4H-cyclopenta[b]thiophene (XI)*. To 1.5 g (0.040 mol) of sodium borohydride in 50 ml of water was, with ice-cooling and rapid stirring, added in small portions 1.5 g (5.3 mmol) of X. After the addition was complete, the stirring was continued till most of the solid had dissolved (~1 h). After filtration, the solution was cautiously acidified with dilute acetic acid. The organic material was extracted with ether, the ether extract washed with aqueous sodium bicarbonate and water, and then dried over magnesium sulphate. The solvent was evaporated under reduced pressure, giving a brown, oily residue. The oil was taken up in pentane and treated with activated charcoal, whereby a colourless solution was obtained. After standing overnight at –15°, white to faint yellow crystals, m.p. 31–32°, were deposited. The yield of crystalline product was 0.60 g (66 %). NMR, see Table 1. IR (KBr): OH- and C=O-bands absent,  $\text{NO}_2$ -bands at 1550 and 1370  $\text{cm}^{-1}$ . MS (*m/e*, %): 169, 7 % ( $\text{M}^{\oplus}$ ); 122, 100 %. [Found: C 49.49; H 8.37; N 8.30; S 19.5. Calc. for  $\text{C}_7\text{H}_7\text{NO}_2\text{S}$  (169.2): C 49.68; H 8.17; N 8.28; S 18.95.]

*5,6-Dihydro-4H-cyclopenta[b]thiophene-5-one (XII)*. Method A. When the filtered solution in the experiment above was not acidified with acetic acid, but instead dropped



into concentrated hydrochloric acid at  $-15^{\circ}$  with vigorous stirring, a semi-solid substance was deposited. After addition of water, the solid was taken up in ether and the aqueous phase extracted with ether. The combined ether phases were washed with bicarbonate solution and water, and then dried ( $\text{MgSO}_4$ ). Evaporation of the ether gave 0.55 g (75 %) of the crude ketone as brown crystals, m.p.  $90-100^{\circ}$ , with the characteristic smell of indanone. Sublimation at 0.05 mm Hg and subsequent crystallization from hexane (refrigerator) gave 0.30 g (40 %) of an analytical sample, m.p.  $100-101^{\circ}$ , as faint yellow crystals. NMR, see Table I. IR (KBr): C=O:  $1750\text{ cm}^{-1}$  (s) and  $1705\text{ cm}^{-1}$  (v), (in  $\text{CCl}_4$  solution): C=O:  $1767\text{ cm}^{-1}$  (s) and  $1725\text{ cm}^{-1}$  (v). MS ( $m/e$ , %): 138, 39 % ( $\text{M}^{\oplus}$ ); 110, 100 % ( $\text{M}^{\oplus} - \text{CO}$ ). [Found: C 60.3; H 4.60; S 22.7. Calc. for  $\text{C}_7\text{H}_6\text{OS}$  (138.2): C 60.84; H 4.38; S 23.21.].

*Method B.* The mixture of VII and VIII, 2.0 g (0.011 mol), obtained from VI, was added in small portions to a solution of 10 g of stannous chloride dihydrate in 25 ml of 6 N hydrochloric acid, cooled to  $-10^{\circ}$ . After the addition was complete, the stirring was continued for half an hour at  $0^{\circ}$ . 200 ml of water was then added and the organic material extracted with ether. A crystalline product, 0.60 g (40 %), identical (IR, NMR) with the ketone above, was isolated.

*Method C.* When the potassium nitronate, VI, was treated according to method B, the usual work-up gave a 50 % yield of XII.

The melting points are uncorrected. The IR spectra were recorded on a Perkin Elmer grating infrared spectrophotometer type 257, the NMR spectra on a Varian A 60 (with TMS as an internal standard). The elementary analyses were carried out at the Analytical Department, Chemical Center, University of Lund. The MS spectra were obtained with an LKB 9000 with an ionization energy of 70 eV and a direct inlet system.

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