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5-BROMO- AND 5-CHLORO-3-THIOLENE-2-ONE

ALLYLIC REARRANGEMENT IN 5-BROMO-3-THIOLENE-2-ONE

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Abstract—5-Bromo- and 5-chloro-3-thiolene-2-one have been prepared by acid-catalysed dealkylation of 5-bromo- and 5-chloro-2-t-butoxythiophene, respectively. On storage in the liquid state at −20°, 5-bromo-3-thiolene-2-one undergoes allylic rearrangement to 3-bromo-3-thiolene-2-one. At room temperature 5-bromo-3-thiolene-2-one rapidly decomposes to a black tar with formation of a mixture of products among which 3-bromo-3-thiolene-2-one, 3-thiolene-2-one, hydrogen bromide, and hydrogen sulphide have been identified. The NMR spectra of 5-bromo- and 5-chloro-3-thiolene-2-one in CCl_4 show that they exist almost exclusively as such, and have been analysed according to the ABX case. From the theoretical spectra it is deduced that $J_{AX}(J_{34})$ and $J_{BX}(J_{45})$ are of the same sign.

INTRODUCTION

IN EARLIER works[1,2] on substituted thiolene-2-ones unsuccessful attempts to prepare 5-bromo-3(and/or 4)-thiolene-2-one (5-bromo-2-thienol) by dealkylation of 5-bromo-2-t-butoxythiophene[1,2] and by hydrogen peroxide cleavage of 5-bromo-2-thiopheneboronic acid[2] have been reported. At that time NMR spectra of our compounds were recorded at the University of Copenhagen and the NMR spectrum of the assumed 5-bromo-2-thienol (CCl_4) (Fig. 1), recorded three days after isolation (distillation), showed three very complex bands near δ 7·6 ppm, 6·3 ppm and 4·1 ppm and a singlet at δ 3·08 ppm with poor relations in the integrated intensities. Analysis of the spectrum

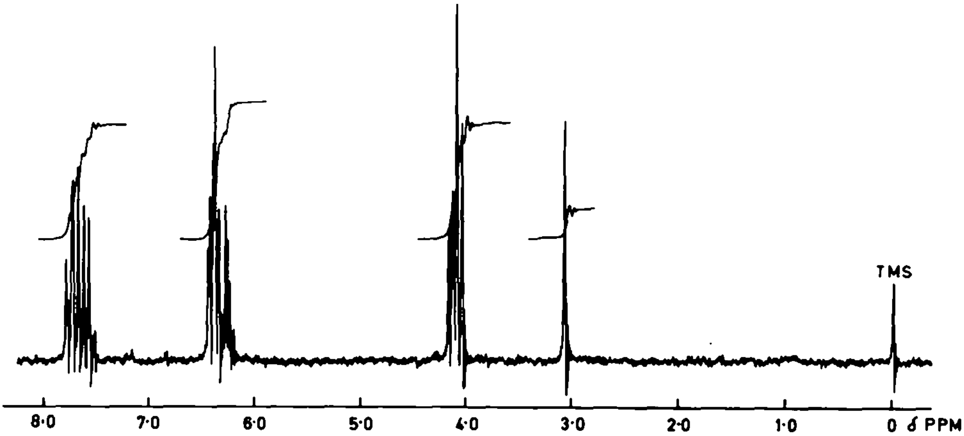

FIG. 1 NMR spectrum of 5-bromo-2-thienol (CCl_4) recorded three days after isolation.

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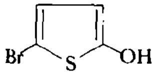
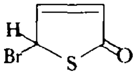
[1] H. J. Jakobsen, E. H. Larsen and S.-O. Lawesson, *Tetrahedron* **19**, 1867 (1963).

[2] A.-B. Hörnfeldt and S. Gronowitz, *Arkiv Kemi* **21**, 239 (1963).

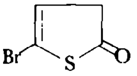
showed that the complexity, chemical shifts and integrated intensities could not be accounted for by the possible presence of a mixture of tautomers (I, II and III) for which reason it was declared impure. Furthermore it was found that the compound is very unstable and decomposes to a tarry mass with evolution of hydrogen bromide and hydrogen sulphide on standing at room temperature.



I



II



III

The origin of the complexity in the observed NMR spectrum has now been identified and the NMR spectra of pure 5-bromo-3-thiolene-2-one and 5-chloro-3-thiolene-2-one have been obtained.

RESULTS AND DISCUSSION

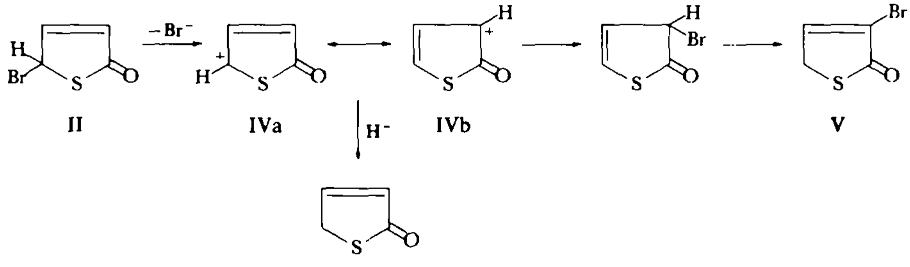
It was found that redistillation of a sample of 5-bromo-3(and/or 4)thiolene-2-one (original b.p. 60–63°/0·1 mm) which had darkened on standing at room temperature for 6 days gave a much lower boiling fraction (b.p. 44–50°/0·1 mm) along with a second fraction of b.p. 50–70°/0·1 mm; a tarry residue was left in the distillation flask. The low boiling fraction was identified as almost pure 3-thiolene-2-one (VI)[1] (2-thienol) on the basis of its NMR and IR spectra; the NMR spectrum (CCl_4 soln) shows 3 bands: a doublet of triplets at δ 7·55 ppm (1 H), another doublet of triplets δ 6·25 ppm (1 H) and finally a doublet of doublets at δ 4·10 ppm (2 H) with coupling constants in accordance with values obtained earlier.[1] The NMR spectrum (CCl_4) of the second fraction shows 3 bands of almost similar complexity, same chemical shifts but different intensities as compared with the spectrum in Fig. 1. It could, however, now easily be recognized that these spectra also show the presence of 3-thiolene-2-one; furthermore a doublet at δ 4·08 ppm with $J \approx 3$ c/s is partly overlapping the doublet of doublets at δ 4·10 ppm (CH_2 protons in 3-thiolene-2-one) in both spectra.

A second observation was that an original sample ($\sim$200 mg) of 5-bromo-2-thienol[1] after being stored in the liquid phase at $-20°$ for two years had rearranged almost completely to a crystalline compound with m.p. 81–82°; NMR and IR spectra show that the rearranged compound is 3-bromo-3-thiolene-2-one (V). The NMR spectrum (CCl_4) consists of a 1 :2 :1 triplet at δ 7·71 ppm (1 H) and a doublet at δ 4·07 ppm (2 H) with $J_{45} = 3·1$ c/s. These data, IR spectrum, and m.p. are in accordance with earlier published data.[2]

On this basis the doublet at δ 4·08 ppm in the above mentioned complex spectra of the original samples of 5-bromo-2-thienol has been assigned to the CH_2 protons in 3-bromo-3-thiolene-2-one (V), resulting from rearrangement. It is now evident that the complexity in the 3 bands of the original spectrum (Fig. 1) arises from overlap of signals from at least 5-bromo-2-thienol, 3-bromo-3-thiolene-2-one (V), and 3-thiolene-2-one (VI). From considerations of the chemical shifts and intensities of the three bands (Fig. 1) it is furthermore concluded that 5-bromo-2-thienol exists as 5-bromo-3-thiolene-2-one (II), and that two of its protons (presumably H_3 and H_5) occur in the band near δ 6·3 ppm, and the third near δ 7·6 ppm (ABX spin system).

The absence of signals from the tautomeric 5-bromo-4-thiolene-2-one form (III) in the NMR spectrum (a doublet for the CH_2 protons should occur near δ 3·3 ppm[1,3] if III is present) is surprising since it is the first known 5-substituted thiolene-2-one[1,3] in which the 4-thiolene-2-one form can not be detected by NMR spectroscopy.

The formation of 3-bromo-3-thiolene-2-one from 5-bromo-3-thiolene-2-one may be explained as due to an allylic rearrangement through the carbonium ions IVa and IVb. Addition of a hydride ion to one of these carbonium ions accounts for the formation of 3-thiolene-2-one (VI) (both V and VI are the tautomers of lowest energy).



It has, however, not yet been possible to identify the corresponding product of oxidation but it only gives rise to a singlet at δ 3·08 ppm (CCl_4) in the NMR spectrum (see below).

In order to analyse the ABX spectrum of 5-bromo-3-thiolene-2-one (II) and to follow the increase in signals due to the rearrangement product V and reduction-oxidation products new attempts have been made to isolate II in a pure state. Pyrolytic elimination of isobutylene from 5-bromo-2-t-butoxythiophene at 160° immediately followed by fractionation gives an almost colourless liquid of 5-bromo-3-thiolene-2-one but always in a purity of only about 90%, the remaining 10% being mainly 3-thiolene-2-one and only a little of the oxidation product (singlet at δ 3·08 ppm); most of the oxidation product is believed to be left in the tarry residue in the distillation flask. However, when this fraction of 5-bromo-3-thiolene-2-one was placed in a dry ice-ethanol bath (−70°) for a few minutes and then placed in a refrigerator at −20° it crystallized. 5-bromo-3-thiolene-2-one was now obtained in a state of at least 98% purity, as indicated by its NMR spectrum (CCl_4), by washing the crystals with a little cold CCl_4 followed by immediate filtering. The colourless crystals of 5-bromo-3-thiolene-2-one had m.p. 25–26°. After storage of the NMR sample tube solution (CCl_4) for 5 days crystals appeared in the solution. After filtering, the solution was examined by NMR and showed a strong increase in the compounds V and VI but only a very weak singlet at δ 3·08 ppm due to the oxidation product. The integrated intensities of the three complex bands agreed with the presence of signals only from II, V and VI in these bands and in the ratio of about 5 :1 :1, respectively. Therefore the crystals formed on storage in CCl_4 are identical with the oxidation product and when examined by NMR ($(CD_3)_2SO$) they only show a singlet at δ 2·92 ppm.

The ABX spectrum of pure 5-bromo-3-thiolene-2-one in CCl_4 (Fig. 2a) has an uncommon appearance as only 5 lines are observed in the AB part of the spectrum.

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[3] A.-B. Hörnfeldt, *Arkiv Kemi* **22**, 211 (1964).

This is due to the fact that one of the two usually occurring AB-type quartets for the AB part of an ABX spectrum has collapsed to a single line (the 2,4,6,8 quartet). Analysis of the spectrum according to Pople *et al.*,[4] using the observable parameters $|J_{AB}| = 1{\cdot}2$ c/s, $|J_{AX} + J_{BX}| = 9{\cdot}0$ c/s, $2D_+ = 1{\cdot}2$ c/s and $2D_- = 3{\cdot}3$ c/s, gave the values listed in Table 1 for the coupling constants and chemical shifts.

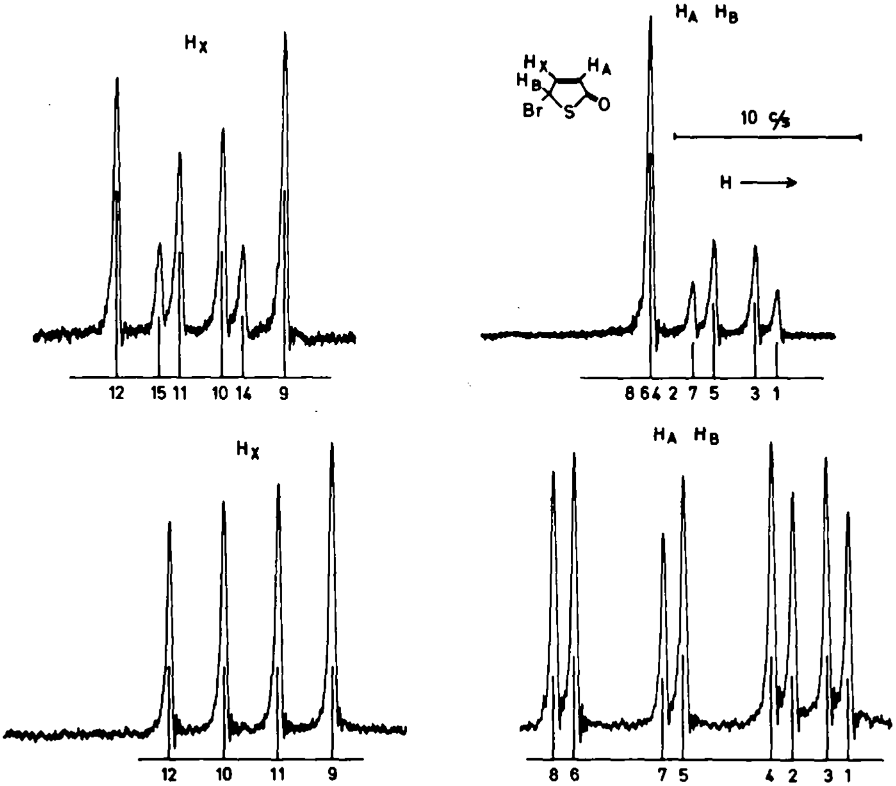

FIG. 2 ABX Spectra of 5-bromo-3-thiolene-2-one (II) in CCl_4 (a) and C_6D_6 (b) together with the spectra calculated[4] from the data in Table 1 for J_{AX} and J_{BX} having the same sign.

Apart from the somewhat smaller value for J_{AB} and from the low field shift of proton H_B these values are all in accordance with the values for other substituted 3-thiolene-2-ones.[1-3] Furthermore a good agreement is found with the coupling constants in 4-bromocyclopent-2-en-1-one ($J_{34} = 3{\cdot}0$ c/s and $J_{24} = \pm\, 1{\cdot}3$ c/s).[5] Calculation of the theoretical spectrum (Fig. 2a) proves J_{AX} and J_{BX} to be of the same sign (using J_{AX} and J_{BX} with opposite sign results in $\cos 2\varphi_+ > 1$). Another interesting feature is found in the X part of the spectrum since the combination lines (the transitions 14 and 15), which usually are very weak or may even not be observed, occur as rather strong lines due to the small value for $\Delta\nu_{AB}$. Using C_6D_6 as solvent the spectrum has a quite different appearance (Fig. 2b): the AB part clearly shows two AB-type quartets and the combination lines 14 and 15 in the X part have completely disappeared due

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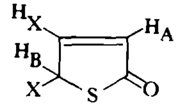
[4] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* Chap. 6, McGraw-Hill, New York (1959).

[5] E. W. Garbisch, Jr., *J. Am. Chem. Soc.* **86**, 5561 (1964).

TABLE 1. COUPLING CONSTANTS (c/s AND CHEMICAL SHIFTS (δ ppm) OBTAINED FROM ANALYSIS OF THE ABX SPECTRA OF



X	$\lvert J_{AX}\rvert$	$\lvert J_{BX}\rvert$	$\lvert J_{AB}\rvert$	$\Delta\nu_{AB}{}^{c}$	δ_A	δ_B	δ_X
Br^{a}	6·1	2·9	1·2	−1·6	6·37	6·34	7·61
Br^{b}	5·8	3·0	1·1	+10·2	5·68	5·51	6·66
Cl^{a}	6·0	2·8	1·3	+0·3	6·37	6·37	7·51

[a] CCl_4 as solvent. [b] C_6D_6 as solvent. [c] $\Delta\nu_{AB}$ positive for H_A at lower field than H_B; obtained at 60 Mc/s.

to the increase in $\Delta\nu_{AB}$. The result of the analysis in this case from the parameters $|J_{AB}| = 1{\cdot}1$ c/s, $|J_{AX} + J_{BX}| = 8{\cdot}8$ c/s, $2D_+ = 11{\cdot}6$ c/s and $2D_- = 8{\cdot}8$ c/s is given in Table 1 and the calculated spectrum in Fig. 2b for J_{AX} and J_{BX} having the same sign. It was interesting to note that II is quite unaltered when stored for a month in this solvent.

5-Chloro-3-thiolene-2-one, prepared by dealkylation of 5-chloro-2-t-butoxythiophene, seems to be more stable than its bromo analogue as no rearrangements were observed even after a month; however, the compound becomes intensely red on storage at −20°.

The NMR spectrum of 5-chloro-3-thiolene-2-one in CCl_4 (Fig. 3) is also an interesting ABX spectrum with two separated AB-type quartets in the AB part and 6 strong lines in the X part. The analysis was carried out using the parameters $|J_{AB}| = 1{\cdot}3$ c/s, $|J_{AX} + J_{BX}| = 8{\cdot}8$ c/s, $2D_+ = 2{\cdot}2$ c/s and $2D_- = 1{\cdot}8$ c/s, and the results are given in Table 1. The very small chemical shift difference for the protons A and B ($\Delta\nu_{AB} = 0{\cdot}3$ c/s) causes an exceptional feature in the X spectrum as the combination lines 14 and 15 occur as lines with medium intensity. Calculation of the theoretical spectrum (Fig. 3) shows J_{AX} and J_{BX} to be of the same sign as for the bromo analogue.

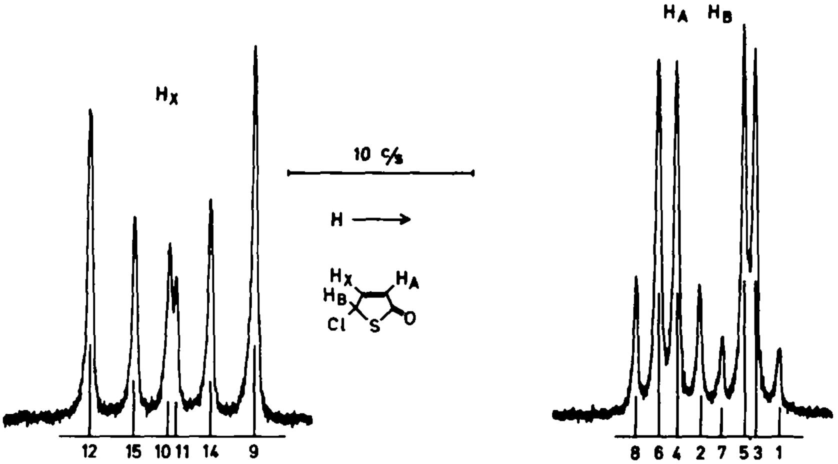


FIG. 3 ABX Spectrum of 5-chloro-3-thiolene-2-one in CCl_4 together with the theoretical spectrum calculated from the data in Table 1 and for J_{AX} and J_{BX} having the same sign.

The NMR spectrum, recorded on the day of isolation of the compound, also showed the presence of the tautomeric 5-chloro-4-thiolene-2-one form but it only constitutes 2% of the total mixture. The methylene protons show up as a doublet at δ 3·55 ppm with J_{34} = 2·9 c/s and the corresponding triplet for the ethylenic proton was located at δ 5·85 ppm by means of time averaging computing. In a NMR spectrum of a sample which had been stored at −20° for a month it was not possible to detect the 5-chloro-4-thiolene-2-one tautomer any longer and it was further noted that no rearrangement products had been formed.

IR spectra of 5-bromo- and 5-chloro-3-thiolene-2-one show C=O stretching frequencies at 1710 and 1700 cm^{-1} which is a shift towards higher frequencies compared with the values for hitherto studied 3-thiolene-2-ones (1695–1665 cm^{-1}).[1-3] Furthermore, both compounds show strong bands at 800 cm^{-1}, the region characteristic for 3-thiolene-2-ones (805–790 cm^{-1}).[3]

EXPERIMENTAL

NMR spectra of the 20% (v/v) solns were recorded at 60 Mc/s on a Varian A-60 spectrometer. The parameters used for the analysis of the spectra were measured with an accuracy of ±0·1 c/s on the 50 c/s scale. The temp in the probe was 33° ± 2°. Time average computing was carried out using the Varian C-1024 Time Averaging Computer. IR spectra were recorded on a Beckman IR 10. Analyses were made by the analytical laboratory at this Institute. B.ps and m.ps are uncorrected.

5-*Bromo*-2-*t*-*butoxythiophene* was prepared according to Ref. 1.

5-*Chloro*-2-*t*-*butoxythiophene*. Ethereal n-BuLi (0·26 mole; 195 ml 1·35 N) was added dropwise to 2-chlorothiophene (29·8 g, 0·25 mole) in 100 ml dry ether and the mixture refluxed during 5 hr. The Li-reagent was added rapidly under N_2 to an ethereal soln of anhyd $MgBr_2$ [prepared by dropping Br_2 (0·31 mole, 50 g, 15·7 ml) to Mg (0·41 g-atoms, 9·5 g) in 200 ml anhyd ether; excess Mg was removed by filtration under N_2], and the mixture stirred for ½ hr at room temp. t-Butyl perbenzoate (0·23 mole, 46 ml) in 75 ml dry ether was added dropwise to the Grignard reagent at 0° and stirring continued for 2 hr. The mixture was worked up as described for the bromo analogue[1] and dried (Na_2SO_4). The ether was removed and distillation *in vacuo* gave a light-yellow liquid with b.p. 38–40°/0·1 mm; redistillation gave an almost colourless liquid b.p. 37–38°/0·1 mm; n_D^{20} = 1·5102; yield 31·6 g (72%). (Found: C, 50·44; H, 5·88; Calc.: C, 50·39; H, 5·82%).

5-*Bromo*-3-*thiolene*-2-*one* (II). 5-Bromo-2-t-butoxythiophene (24·8 g, 0·106 mole) was placed in a 25 ml distillation flask and dealkylated at 160° (oil bath) in the presence of 0·1 g *p*-toluenesulphonic acid. After the evolution of isobutylene had ceased (5–10 min) the product was *immediately* distilled under N_2, giving a slightly coloured liquid of about 90% pure 5-bromo-3-thiolene-2-one with b.p. 60–65°/0·1 mm; yield 14·5 g. The compound was immediately placed in a dry ice-EtOH bath (−70°) for a few min and then placed in a refrigerator at −20° in order to crystallize. After washing a part of these crystals with a little cold CCl_4 and immediate filtration, 5-bromo-3-thiolene-2-one was obtained as colourless crystals with m.p. 25–26°. (Found: C, 27·04; H, 1·69; Calc.: C, 26·84; H, 1·69%). Avoid contact with the skin as it colours it intensely black.

5-*Chloro*-3-*thiolene*-2-*one*. 5-Chloro-2-t-butoxythiophene (20·8 g, 0·109 mole) was dealkylated as described above. Colourless liquid with b.p. 45–47°/0·1 mm; n_D^{20} = 1·5704; yield 12·4 g (84%). (Found: C, 35·92; H, 2·35; Calc.: C, 35·70; H, 2·25%).

3-*Bromo*-3-*thiolene*-2-*one* (V). A sample (~200 mg) of 90% pure 5-bromo-3-thiolene-2-one was kept in the *liquid* state at −20° for 2 years when 3-bromo-3-thiolene-2-one had crystallized. Recrystallization from cyclohexane gave colourless plates with m.p. 81–82° (litt.[2] m.p. 81–82°).

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