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Metalation of Thieno[2,3-b]thiophene and Thieno[3,2-b]thiophene with Butyllithium

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The metalation of thieno[2,3-b]thiophene and thieno[3,2-b]-thiophene with ethereal butyllithium has been investigated. In both cases the metalation occurred in the α-position. By means of competitive metalation experiments both the thienothiophenes were found to be about 6 times more reactive than thiophene.

Metalation with butyllithium has been studied for a number of years and it has been found that in heterocyclic compounds the hydrogens *ortho* to the hetero atom are usually the ones to be replaced. Thus butyllithium metalates thiophene[1] and thionaphtene[2] in the α-positions, while methyl phenyl sulphide is metalated on the methyl carbon. On the other hand, Goldfarb[3] has found that metalation of 5-methyl-2-thienyl methyl sulphide occurs in the 3-position of the thiophene nucleus.

A survey made by Gilman and Morton[4] in 1954 discusses two different interpretations of mechanisms for metalation with butyllithium. In both mechanisms it is considered that an initial coordination between the metal in the metalating agent and the hetero atom takes place. In one, suggested by Roberts and Curtin,[5] the next step is supposed to be a nucleophilic attack by the carbanion part of the organometallic ion-pair on the adjacent hydrogen removing it as a proton. The other mechanism, proposed by Morton,[6] implies an electrophilic attack on the carbon by the metal cation, removing the hydrogen by a push-pull type of reaction. Bryce-Smith[7] has metalated aromatic hydrocarbons with alkylsodium and -potassium and proposes a mechanism involving a protophilic attack by the metalating agent on the C—H bond forming a four member ring transition state. To show that the elimination of the ring hydrogen can be the rate-determining step, Bryce-Smith *et al.*[8] metalated deuterium labeled benzene and found a k_H/k_D ratio of 1.7—2.5. A similar isotope effect is demonstrated by Gronowitz and Halvarson[9] and Shirley and Barton[10] on deuterium and tritium labeled thiophene.

In order to gain more information about the metalation of the thienothiophenes, thieno[2,3-b]thiophene and thieno[3,2-b]thiophene were metalated

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with butyllithium. Thieno[2,3-b]thiophene was prepared according to Gronowitz and Persson.[11] As a by-product (3-formyl-2-thienylthio)acetic acid was isolated. Thieno[3,2-b]thiophene was synthesized by the procedure of Goldfarb *et al.*,[12] but by using dimethyl formamide instead of dimethyl formanilide in the Vilsmeier formylation, the methyl (2-formyl-3-thienylthio)acetate was isolated in crystalline form. Also here the free acid, (2-formyl-3-thienylthio)-acetic acid, was obtained as a by-product. The two isomeric thienothiophenes have previously been metalated by Challenger *et al.*[13-15] with ethylmagnesium bromide and after carbonation two monoacids, thieno[2,3-b]thiophene-2-carboxylic acid and thieno[3,2-b]thiophene-2-carboxylic acid, and the dicarboxylic acid thieno[3,2-b]thiophene-2,5-dicarboxylic acid have been isolated in small yields. The dicarboxylic acid was only characterised as the dimethylester.

By metalation with one equivalent of butyllithium followed by carbonation the monoacids were obtained in good yields and it was confirmed by comparison with the IR-spectra of the authentic monoacids of thieno[2,3-b]-thiophene and thieno[3,2-b]thiophene that the metalations had occurred in the α-positions. Metalation with two equivalents of butyllithium gave, after carbonation, the dicarboxylic acids which, based on the fact that the NMR-spectra have only one peak in the thiophene region, is considered to be thieno-[2,3-b]thiophene-2,5-dicarboxylic acid and thieno[3,2-b]thiophene-2,5-dicarboxylic acid. No metalations in the β-positions were detected.

To form an opinion about the reactivity of the two isomeric thienothiophenes compared with thiophene, competitive metalation experiments were carried out. Equimolar quantities of thiophene and thieno[2,3-b]thiophene or thieno[3,2-b]thiophene dissolved in ether were metalated with a deficit of butyllithium. The temperature was kept at $25 \pm 1°$ and the reaction time after the addition of the metalating agent was 1 min. The reaction was stopped by hydrolysis with an excess of $CH_3COOD + D_2O$ and the reaction mixture was analysed with a mass spectrometer fitted with a gas chromatograph. The ratio in mole per cent between thiophene and deuterothiophene and between the thienothiophene and the deuterothienothiophene was determined by calculating the ratio between the peaks m/e 84 and 85 and m/e 140 and 141 according to Biemann.[16]

Calculation of the relative reactivities is expressed by the equation[17]

$$k_{TT}/k_T = \log([TT]_i/[TT]_f)/\log([T]_i/[T]_f)$$

where T = thiophene, TT = thieno[2,3-b]thiophene or thieno[3,2-b]thiophene, k = relative rate constant for the metalation reaction with butyllithium and $[\ ]_i$ and $[\ ]_f$ are the initial and final concentrations.

The use of the above equation is based on the assumption that the metalation reaction of thiophene and the thienothiophenes are of the same order and that the analysis of the reaction products will only reflect the forward reaction. To establish the validity of these assumptions the following experiments were performed:

1) The competitive metalations were carried out at three different concentrations but no concentration effect was detected.

2) Transmetalation experiments between 2-thienyllithium and the thienothiophenes and between the two 2-lithiothienothiophenes and thiophene showed that a state of equilibrium between the metalated and unmetalated components in the reaction mixture must exist, but that the rate of transmetalation is so slow that the error introduced will be small compared with the error in the analysis of the reaction mixture.

Because of the slowness of the transmetalation reaction, sidereactions, possibly due to cleavage of the ether,[18] made it impossible to determine the state of equilibrium.

The experimental results show that thieno[2,3-b]thiophene is about 6.2 times more reactive than thiophene and thieno[3,2-b]thiophene is about 5.8 times more reactive. Since these values are of the same order of magnitude a further comparison is impossible without additional experimental evidence.

From the results one can also conclude that the metalation with butyllithium is a kinetically controlled reaction while the transmetalation is thermodynamically controlled.

The NMR-spectra of 2-lithiothieno[2,3-b]thiophene and 2-lithiothieno-[3,2-b]thiophene were recorded and compared with the spectra of the unsubstituted compounds. In both cases one hydrogen shifted down field and, by analogy with earlier investigations,[19,20] it is presumed that they must be the hydrogens situated *ortho* to the lithium. In the spectrum of 2-lithiothieno[3,2-b]thiophene the two hydrogens in the other ring had the same shift and shifted towards higher field relative to the unsubstituted compound. The spectrum of 2-lithiothieno[2,3-b]thiophene was resolved with a coupling between the 4 and 5 hydrogens of 5.2 c/s as expected for the thiophenes. Also here an upfield shift of the protons was noted.

The ring proton spectrum of thieno[3,2-b]thiophene-2-carboxylic acid shows a doublet ($J = 0.6$ c/s) at 1.79 τ, a doublet at 2.04 τ ($J = 5.2$ c/s) and a quartet at 2.44 τ ($J = 5.2$ and 0.6 c/s). By considering the contributing resonance structures for thieno[3,2-b]thiophene-2-carboxylic acid it is possible to assign the lowest field band to hydrogen 3, the next to hydrogen 5, and the quartet band to hydrogen 6. The NMR-spectrum of thieno[3,2-b]thiophene has earlier been analysed by Gestblom *et al.*[21,22] They found two long-range couplings across the rings of the magnitude of 1.5 c/s and 0.75 c/s, but could not decide which was $J_{2,5}$ and $J_{3,6}$, respectively. The present results could indicate, assuming that introduction of the carboxyl group does not change the magnitude of these couplings significantly, that the smaller coupling is between the 3- and 6-hydrogen. Cross-ring couplings of such magnitude was not detected in the spectrum of thieno[2,3-b]thiophene-2-carboxylic acid, only a coupling of 5.6 c/s between the 4- and 5-hydrogen was observed.

EXPERIMENTAL

All the reactions with butyllithium were carried out in the usual Grignard apparatus in a nitrogen atmosphere.

About 1 N ethereal butyllithium was prepared according to Wittig.[23] The normality of the solution was determined by acid titration.

CH_3COOD in D_2O was prepared by hydrolysing 60 g of carefully redistilled acetic anhydride with 20 ml of D_2O (CIBA 99.75 %).

Methyl (3-thienylthio)acetate was prepared according to Goldfarb[12] in about 64 % yield. B.p. 94—96° (0.3 mm). (Lit.value b.p. 110—111° (2 mm)).

Methyl (2-formyl-3-thienylthio)acetate. 176 g (1.15 mole) phosphorus oxychloride was with stirring and external cooling added drop-wise to 84 g (1.15 mole) of N,N-dimethylformamide and stirred for 30 min. To this mixture was added, drop-wise with cooling, 188 g (1.0 mole) methyl (3-thienylthio)acetate and the reaction mixture was stirred for 4 h. The mixture was allowed to stand for 42 h before it was poured onto ice. It is important to keep the reaction mixture below room temperature during the hydrolysis which usually takes 2—3 h. The aqueous phase was extracted several times with ether and the ethereal phase was washed with water, 1:10 hydrochloric acid, saturated sodium bicarbonate solution, water, and dried with anhydrous magnesium sulphate. The ether was removed by distillation, finally in vacuum, to give 111 g (51 %) of crude methyl (2-formyl-3-thienylthio)acetate after washing the crystalline product on the filter with ice-cold methanol. Recrystallization from methanol gave nearly colourless needles melting at 39—40°.

NMR ($CDCl_3$): τ_{CHO} —0.17, τ_5 2.20, τ_4 2.74, $\tau_{CH_2CH_3}$ 6.27. $J_{4,5}$ 5.2 c/s, $J_{CHO,5}$ 1.0 c/s.

Acetone: τ_{CHO} —0.11, τ_5 1.96, τ_4 2.62, τ_{CH_2} 6.10, τ_{CH_3} 6.32. $J_{4,5}$ 5.2 c/s, $J_{CHO,5}$ 1.0 c/s.

(Found: C 44.5; H 3.70; S 29.5. Calc. for $C_8H_8O_3S_2$ (216.3): C 44.42; H 3.73; S 29.65).

The sodium bicarbonate extract was acidified with dilute hydrochloric acid precipitating 18 g of crude (2-formyl-3-thienylthio)acetic acid. Recrystallization from water gave needles, m.p. (decomp.) 166—171° in a sealed capillary.

NMR (DMSO): τ_{CHO} —0.05, τ_5 1.81, τ_4 2.60, τ_{CH_2} 6.04. $J_{4,5}$ 5.2 c/s, $J_{CHO,5}$ 1.0 c/s.

(Found: C 41.4; H 3.15; S 31.6. Calc. for $C_7H_6O_3S_2$ (202.3): C 41.57; H 2.99; S 31.71).

Thieno[3,2-b]thiophene-2-carboxylic acid was prepared by the method described by Goldfarb,[12] giving the acid in yields of about 90 %. M.p. 219—221° in a sealed capillary.

NMR (DMSO): τ_{COOH} 1.36, τ_3 1.79, τ_5 2.04, τ_6 2.44. $J_{5,6}$ 5.2 c/s, $J_{3,6}$ 0.6 c/s.

Thieno[3,2-b]thiophene was synthesized by decarboxylation of the acid in quinoline in the presence of copper bronze according to Goldfarb,[12] with the exception that before acidification the quinoline-thieno[3,2-b]thiophene mixture was purified by distillation under reduced pressure. The thieno[3,2-b]thiophene, m.p. 55—56° was isolated in yields of about 90 %.

Thieno[2,3-b]thiophene-2-carboxylic acid was made according to Gronowitz[11] from 0.6 mole 3-thiophene aldehyde ethylene acetal in a yield of 74 % calculated on the crude product and identified by its IR-spectrum.

NMR (DMSO): τ_3 1.94, τ_5 2.21, τ_4 2.52. $J_{4,5}$ 5.4 c/s.

The sodium bicarbonate extract was acidified with dilute hydrochloric acid precipitating 2.1 g of crude (3-formyl-2-thienylthio)acetic acid. Recrystallization from water gave needles, m.p. 126—137°.

NMR (acetone): τ_{CHO} —0.25, τ_5 2.29, τ_4 2.46. $J_{4,5}$ 5.6 c/s, $J_{CHO,5}$ 0.6 c/s.

(Found: C 41.6; H 3.01; S 31.8. Calc. for $C_7H_6O_3S_2$ (202.3): C 41.57; H 2.99; S 31.71).

Thieno[2,3-b]thiophene was made according to Gronowitz[11] with the exception that instead of refluxing the reaction mixture for 24 h the quinoline-thieno[2,3-b]thiophene mixture was distilled in a nitrogen atmosphere while quinoline was simultaneously being added to the reaction mixture to keep the volume constant. When approximately the same volume of quinoline as that in which the acid was initially dissolved, had been added, the reaction mixture was distilled almost to dryness under reduced pressure. The thieno[2,3-b]thiophene, b.p.$_{15}$ 102.5—104.0°, was isolated in yields of about 80 %. For use in the competitive and the transmetalation experiments the thieno[2,3-b]thiophene was carefully redistilled using a helices packed column.

Metalation of thieno[3,2-b]thiophene with one equivalent of butyllithium. To 3.5 g (0.025 mole) of thieno[3,2-b]thiophene in 25 ml of dry ether, 24.3 ml of 1.03 N ethereal butyllithium was added drop-wise and the mixture refluxed for 30 min. The solution was then poured onto a mixture of Dry Ice and ether. When the Dry Ice had evaporated the mixture was hydrolysed with water. The aqueous phase was extracted once with ether and the combined ether phases twice with sodium bicarbonate solution. The combined aqueous phases were acidified with 2 N hydrochloric acid, precipitating 3.4 g (74 %) of crude thieno[3,2-b]thiophene-2-carboxylic acid, m.p. 216—220° (lit. value[13] 220—220.5°). About 1 ml of the metalated product was drawn into an evacuated NMR-tube and sealed. The NMR-spectrum was recorded at the working temperature (36°) of the NMR-apparatus and had shifts at τ 2.91 and τ 2.48 and in the ratio 2:1. The NMR-spectrum of thieno[3,2-b]thiophene in the same solvent indicated absorptions at τ 2.86, 2.77, 2.69, and 2.58.

Metalation of thieno[3,2-b]thiophene with two equivalents of butyllithium. To 7.0 g (0.05 mole) of thieno[3,2-b]thiophene in 25 ml of dry ether was added drop-wise 110 ml of 1.0 N butyllithium and the mixture refluxed for 1 h. The reaction mixture was carbonated and worked up as described above, giving 10.6 g of acidic material. From the integration of the NMR-spectrum the compound was estimated to contain about 70 % thieno[3,2-b]thiophene-2,5-dicarboxylic acid and 30 % thieno[3,2-b]thiophene-2-carboxylic acid. After recrystallization from dimethyl sulphoxide and treatment of the crystals on the filter with ethanol the thieno[3,2-b]thiophene-2,5-dicarboxylic acid decomposed without melting at 340–350° in a sealed capillary. NMR (DMSO): τ_{COOH} -0.01, $\tau_{3,6}$ 1.85.

(Found: C 42.0; H 2.01; S 27.9. Calc. for $C_8H_4O_4S_2$ (228.2): C 42.10; H 1.77; S 28.10).

Metalation of thieno[2,3-b]thiophene with one equivalent of butyllithium. Treatment of 3.5 g (0.025 mole) of thieno[2,3-b]thiophene with 30.2 ml of 0.83 N ethereal butyllithium, as described above, yielded 3.6 g (78 %) of thieno[2,3-b]thiophene-2-carboxylic acid. M.p. 242–245° (lit. value[15] 245°).

About 1 ml of the metalated product was drawn into an evacuated NMR-tube and sealed. The NMR-spectrum was recorded at the working temperature (36°) of the instrument and had shifts at τ_3 2.50, $\tau_{4\text{ or }5}$ 2.79, $\tau_{4\text{ or }5}$ 2.96. $J_{4,5}$ 5.2 c/s. The NMR-spectrum of thieno[2,3-b]thiophene in the same solvent indicated absorptions at τ 2.61, 2.69, 2.79, 2.87.

Metalation of thieno[2,3-b]thiophene with two equivalents of butyllithium. Treatment of 3.5 g (0.025 mole) of thieno[2,3-b]thiophene with 67 ml of 0.87 N butyllithium, as described above, yielded 4.7 g acidic material. After recrystallization from a large volume of acetic acid the thieno[2,3-b]thiophene-2-carboxylic acid decomposed without melting above 330° in a sealed capillary. NMR (DMSO): $\tau_{3,4}$ 1.90.

(Found: C 42.1; H 1.72; S 26.9. Calc. for $C_8H_4O_4S_2$ (228.2): C 42.10; H 1.77; S 28.10).

General procedure for the competitive and the transmetalations. All the reactions were performed in a four-necked nitrogen swept flask fitted with magnetic stirrer, nitrogen inlet, reflux condenser, dropping funnel, and a glas tube connecting a smaller nitrogen swept flask fitted with stirrer, dropping funnel, and nitrogen inlet. The larger flask was kept at 25 ± 1° in a thermostated water bath.

The competitive metalations were carried out by dissolving the thiophene and thieno[3,2-b]thiophene or thieno[2,3-b]thiophene in absolute ether. To this mixture was added drop-wise during 5 min 0.8 molar equivalent of butyllithium; the reaction mixture was stirred for an additional minute and then transferred with nitrogen pressure into the smaller flask where it was hydrolysed with a large excess of $CH_3COOD + D_2O$. The hydrolysed mixture was treated with water, saturated sodium bicarbonate solution, and water and dried over calcium chloride together with some decolourizing carbon.

The transmetalation experiments were carried out in the same apparatus as described above. One molar equivalent of thiophene, thieno[3,2-b]thiophene or thieno[2,3-b]thiophene, dissolved in absolute ether was metalated with 0.8 molar equivalents of butyllithium and stirred for about 15 min. To this mixture was added, all at once, one molar equivalent of the other component, dissolved in dry ether; aliquots of the solution were transferred (nitrogen) into the smaller flask where they were hydrolysed and worked up as described above. In some experiments aliquots of the reaction mixture were drawn into evacuated ampoules and sealed. These ampoules were broken under nitrogen, hydrolysed and worked up in the usual manner.

Transmetalations

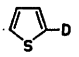
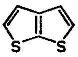
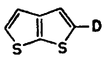
2-Thienyllithium/thieno[2,3-b]thiophene. 2.1 g (0.025 mole) thiophene in about 100 ml of ether was metalated with 18.2 ml (0.020 mole) of 1.10 N butyllithium, giving after hydrolysis 35.3 % thiophene, and 64.7 % 2-d thiophene. 3.5 g (0.025 mole) thieno[2,3-b]thiophene in 50 ml of ether was added and an aliquot of the reaction mixture was kept in a sealed tube for 24 h at 25 ± 1°. The analysis showed 70.8 % thiophene, 29.2 % 2-d thiophene, 74.5 % thieno[2,3-b]thiophene, and 25.5 % 2-d thieno[2,3-b]thiophene.

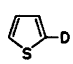
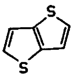
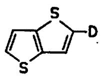
2-Lithiothieno[2,3-b]thiophene/thiophene. In the same manner as above when 0.0125 mole thieno[2,3-b]thiophene in 25 ml of ether was treated with 0.010 mole butyllithium, the analysis showed 37.5 % thieno[2,3-b]thiophene and 62.5 % 2-d thieno[2,3-b]thiophene. After addition of 0.0125 mole thiophene in 25 ml of ether and keeping the reaction mixture for 22 h at 25 ± 1°, the analysis showed 97.5 % thiophene, 2.5 % 2-d thiophene, 44.1 % thieno[2,3-b]thiophene, and 55.9 % 2-d thieno[2,3-b]thiophene.

2-Thienyllithium/thieno[3,2-b]thiophene. 2.1 g (0.025 mole) of thiophene in about 100 ml of ether was metalated with 17.4 ml (0.020 mole) of 1.15 N butyllithium and showed after hydrolysis 40.6 % thiophene and 59.4 % 2-d thiophene. 3.5 g (0.025 mole) of thieno[3,2-b]thiophene in 50 ml of ether was added and the reaction mixture kept for 22 h at 25 ± 1°. The analysis showed 67.7 % thiophene, 32.3 % 2-d thiophene, 78.7 % thieno[3,2-b]thiophene, and 21.3 % 2-d thieno[3,2-b]thiophene.

2-Lithiothieno[3,2-b]thiophene/thiophene. In the same manner as above when 0.025 mole thieno[3,2-b]thiophene in 100 ml of ether was treated with 17.4 ml (0.020 mole) of 1.15 N butyllithium followed by hydrolysis, the analysis showed 40.4 % thieno[3,2-b]thiophene and 59.6 % 2-d thieno[3,2-b]thiophene. After addition of 0.025 mole of thiophene in 50 ml of ether the reaction mixture were kept for 48 h at 25 ± 1° in a sealed tube. The analysis showed 96.7 % thiophene, 3.3 % 2-d thiophene, 55.9 % thieno[3,2-b]thiophene, and 44.1 % 2-d thieno[3,2-b]thiophene.

Competitive metalations

Vol. of ether in ml after mixing the reactants	Moles of thiophene and of thieno[2,3-b]thiophene	Mole per cent composition of products				k_{TT}/k_T
						
30	0.0125	88.7	11.3	46.5	53.5	6.4
180	0.025	88.1	11.9	44.4	55.6	6.4
210	0.0125	89.0	11.0	50.4	49.6	5.9
					Average	6.2

Vol. of ether in ml after mixing the reactants	Moles of thiophene and of thieno[3,2-b]thiophene	Mole per cent composition of products				k_{TT}/k_T
						
30	0.0125	88.1	11.9	49.0	51.0	5.6
55	0.00625	89.4	10.6	50.2	49.8	6.1
210	0.0125	89.7	10.3	54.0	46.0	5.7
					Average	5.8

Mass-spectra

The mass-spectra were obtained on an LKB 900 mass spectrometer fitted with a gas chromatograph. The column was packed with 5 % neopentyl glycol succinate on Chromosorb W (HMDS) and the temperature was kept at 55° for the thiophenes and at

170° for the thienothiophenes. The temperature of the ion source was 290° and the ionizing potential was kept at 15 eV. The ratios between the deuterated and undeuterated compounds were determined according to Biemann.[16] Different parts of the chromatographic peak were investigated but no isotopic fractionation was detected. Based on a large number of measurements, it was found that the values were reproducible within ± 1 mole per cent.

The NMR-spectra were obtained on a Varian Associates A 60 model NMR-spectrometer. The IR-spectra were recorded on a Perkin-Elmer 257 infrared spectrophotometer.

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