

ON THE STABILITY OF 3-BENZO[b]THIENYL-LITHIUM

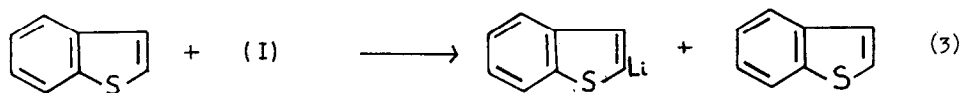
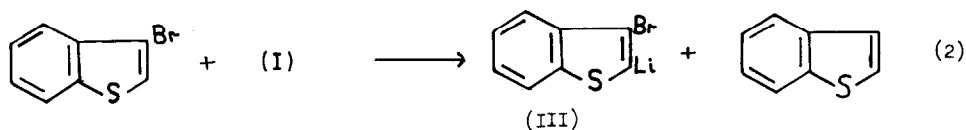
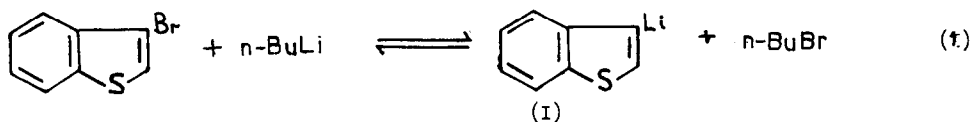
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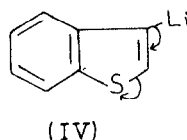
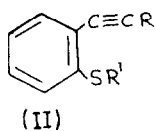
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Recently we¹ reported the synthesis and some reactions of 3-benzo[b]thienyl-lithium (I). When an ethereal solution of (I) was treated at -70° successively with carbon dioxide and acid or with dimethyl sulphate, it gave high yields of benzo[b]thiophen-3-carboxylic acid and 3-methylbenzo[b]thiophen, respectively. A similarly prepared solution of (I) stirred at 20° for 30 min. prior to carbonation gave benzo[b]thiophen-2-carboxylic acid and 3-bromobenzo[b]thiophen-2-carboxylic acid as the major products together with a trace of benzo[b]thiophen-3-carboxylic acid. At that time we believed¹ that the behaviour of (I) in ether paralleled the reported² behaviour of 3-thienyl-lithium in ether and, consequently, that reactions (1) \rightarrow (3) were predominantly responsible for the formation of the above mixture of acids.



Surprisingly, however, a mixture of *o*-(methyl-thio)phenylacetylene (IIa) (4%), methyl *o*-(methylthio)phenylacetylene (IIb) (43%), benzo[b]thiophen (48%), and 3-bromo-2-methylbenzo[b]thiophen (5%) was obtained when an ethereal solution of (I) was prepared at -70° , stirred at 20° for 1 hr., and then treated with an excess of dimethyl sulphate.



- a., R = H, R' = Me d., R = H, R' = Li
b., R = R' = Me e., R = R' = Li
c., R = Me, R' = Buⁿ f., R = CO₂Li, R' = Li

Benzo[b]thiophen and the acetylene (IIb)[†], b.p. 159-160°/28 mm., ν_{\max} (liquid) 2205, 2230, and 2255 cm.⁻¹ (C:C), τ (CCl₄) 7.90 (:CMe), 7.62 (SMe), and 2.6-3.2 (aromatic), and \bar{M} (mass spectrometry) 162 were isolated by chromatography. 3-Bromo-2-methylbenzo[b]thiophen was prepared unambiguously (100% yield) by treating 3-bromo-2-benzo[b]thienyl-lithium (III)³ with dimethyl sulphate, but an attempt⁴ to prepare (IIa) unambiguously gave an impure product. However, it had the same g.l.c. retention time as the product mentioned above and the expected spectroscopic properties, ν_{\max} (liquid) 3290 cm.⁻¹ (:CH), τ (CCl₄) 6.65 (:CH) and 7.65 (SMe), and \bar{M} (mass spectrometry) 148 (the base peak at \bar{m}/e 133 corresponded to loss of CH₃). After stirring an ethereal solution of (I) at 20° for 18 hr. prior to methylation, in addition to benzo[b]thiophen (54%), (IIa)(1%), and (IIb)(25%), we also obtained ^{methyl}o-(n-butylthio)phenylacetylene (IIc)(20%).

For comparison purposes we prepared an ethereal solution of (I) at -70°, stirred it at 20° for 30 min., and then treated one half of it with dimethyl sulphate and the other half successively with carbon dioxide and acid. The former reaction gave a mixture of (IIa), (IIb), benzo[b]thiophen, and 3-bromo-2-methylbenzo[b]thiophen (see above) whilst the latter reaction gave a mixture of benzo[b]thiophen-2-carboxylic acid and 3-bromobenzo[b]thiophen-2-carboxylic acid. Clearly therefore the same intermediates are involved in both processes.

We conclude that (I) is unstable in ether at temperatures much in excess of -70° and undergoes a ring-opening reaction (IV) to give the acetylene (IId), which is metallated by (I) to give the acetylene (IIe) and benzo[b]thiophen. The acetylenes (IId) and (IIe) react with dimethyl sulphate to give (IIa) and (IIb), respectively. The acetylene (IIc)

† With the exception of (IIa) all new compounds analysed correctly for C and H.

presumably arises by alkylation of (IIe) at sulphur by the n-butyl bromide liberated in reaction (1) prior to the mixture being quenched with dimethyl sulphate. The small amount of 3-bromo-2-methylbenzo[b]thiophen formed is assumed to arise by reaction (2). Detailed product studies⁴ following a number of reactions carried out under different conditions confirmed the above conclusions and excluded a number of other reactions. In particular, the failure to detect 2-methylbenzo[b]thiophen in any of our products excluded the occurrence of reaction (3). To explain the results of the carbonation experiments we suggest that the intermediate (IIe) reacts with carbon dioxide to give (IIf) and that the *o*-mercaptophenylpropionic acid derived from (IIf) following the addition of acid to the mixture cyclises to give benzo[b]thiophen-2-carboxylic acid. Cyclisation of (IIf) prior to acidification would be expected to give rise to benzo[b]thiophen-2,3-dicarboxylic acid which was not detected. The absence of *o*-mercaptophenylacetylene [which would be expected to arise from (IIe)] in our products suggests that it also cyclises to give benzo[b]thiophen. The amounts of benzo[b]thiophen present in the products could not be accounted for by accidental hydrolysis of (I) alone nor by the occurrence of reaction (2). In support of this suggestion we prepared an ethereal solution of (I) at -70° stirred it at 20° for 30 min., and then treated one half of it with dimethyl sulphate and the other half with acid. In the former case we obtained the expected mixture of compounds whilst in the latter case the product was a mixture of benzo[b]thiophen and 3-bromobenzo[b]thiophen.

Other 3-benzo[b]thienyl-lithium compounds were found to behave similarly.⁴ Thus, when an ethereal solution of 2-methyl-3-benzo[b]thienyl-lithium was prepared at -70°, stirred at 20° for 1 hr., and then treated with dimethyl sulphate, it gave (IIb)(83%). A similar solution stirred at 20° overnight and then treated with acid gave 2-methylbenzo[b]thiophen (40%) and (IIc)(60%), ν_{\max} : (liquid) 2205, 2230, and 2255 cm^{-1} (C:O), γ (CCl_4) 2.60-3.20 (aromatic), 7.92 (:CMe), 7.13 (α), 8.10-8.90 (β and δ), 9.09 (δ)($\overset{\alpha}{\text{S}}(\overset{\beta}{\text{C}}\overset{\gamma}{\text{H}}_2\overset{\delta}{\text{C}}\overset{\delta}{\text{H}}_2\overset{\delta}{\text{C}}\overset{\delta}{\text{H}}_3)$), and 7.92 (:CMe), and M (mass spectrometry) 204.

Our results suggest that carbon dioxide is an unsuitable quenching reagent for a study of the behaviour of organolithium compounds. Interestingly, Moses and Gronowitz² reported that "unsaturated aliphatic products" arise when an ethereal solution of 3-thienyl-lithium is allowed to stand at 20° for 24 hr. It now

appears likely that these products were acetylenes formed by a ring-opening reaction similar to the one which we now describe.

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References

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2. F. Moses and S. Gronowitz, Arkiv Kemi, 18,119 (1962); S. Gronowitz, Adv. Heterocyclic Chem., 1,75 (1963).
3. W. Ried and H. Bender, Chem. Ber., 88, 34 (1955).
4. Details will be given in a forthcoming publication.