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LITHIATION OF 1,3-DITELLUROLES.
A STRIKING SUBSTITUENT EFFECT OF THE PHENYL GROUP

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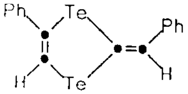
Summary: 1,3-Ditellurole was regiospecifically lithiated at the 4-position by lithium diisopropylamide, whereas 4-phenyl-1,3-ditellurole was regiospecifically lithiated at the 2-position under identical conditions, as shown by subsequent capture of the anions with various electrophiles.

The anions of 1,3-dithioles have been elaborated to various dithia-[1-3] and tetrathiafulvalenes.[2,4] Surprisingly, the direct metalation of 1,3-dithioles has been described only for 1,3-benzodithioles.[5] Other metalations have involved 2-(O,O-dimethylphosphonyl) or 2-tributylphosphonium substituted 1,3-dithioles.

The recent preparation of various 1,3-ditelluroles (**1**[6] and **2**[7]) and the first reports of tetratellurofulvalenes (**3**[8] and **4**[9]) prompted us to investigate the metalation of the 1,3-ditellurole nucleus. We wish to report the strikingly different lithiations of 1,3-ditellurole (**2a**) and 4-phenyl-1,3-ditellurole (**2b**) with lithium diisopropylamide (LDA), as ascertained from the reactions of the lithio derivatives with various electrophiles.



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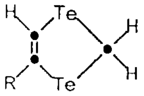
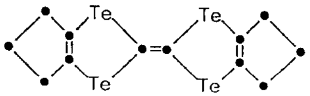


2a, R = H
b, R = Ph



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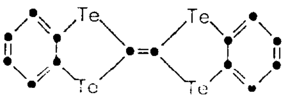
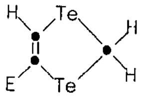


4

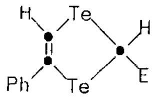
The addition of **2a** to 1.1 equivalents of LDA in tetrahydrofuran (THF) at -70°C (or the addition of 1.1 equivalents of LDA to **2a** in THF at -70°C) gave an orange-yellow solution. The addition of CH_3OD or benzaldehyde at -70°C gave immediate reaction to produce **5a** and **5b**, respectively, in 95% and 77% yields.[10] The addition of CH_3I at -70°C gave no detectable reaction. However, the addition of 5 equivalents of hexamethylphosphoric triamide (HMPTA) gave methylation product **5c** in 40% yield after 0.5 h (as well as 30% of unreacted starting material).

The reactions of **2b** with LDA gave much different results. Capture of the anion generated by LDA with CH_3OD, benzaldehyde, or CH_3I in THF at -70°C gave

6a, 6b, and 6c in 91%, 70%, and 68% yields, respectively. Products derived from lithiation at the 4-position were not detected. HMPTA was not required for the reaction with CH_3I. Presumably, species 6d is formed with LDA.



5a, E = D
b, E = PhCHOH
c, E = CH_3
d, E = Li

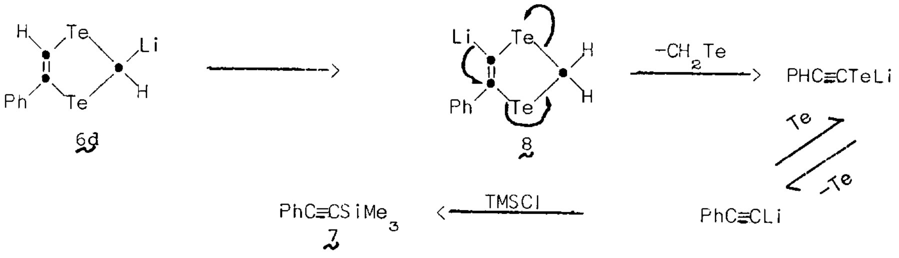


6a, E = D
b, E = PhCHOH
c, E = CH_3
d, E = Li

Attempts to equilibrate the 2-lithio and 4-lithio derivatives by warming the -70°C solutions were unsuccessful. Upon warming, both anions were unstable, giving decomposition products before capture by electrophiles.

Trimethylsilyl chloride (TMSCl) did not react with 6d at -70°C. However, warming a solution of this anion and TMSCl to -20°C gave phenyltrimethylsilylacetyle (7) in 65% yield and tellurium metal. The formation of 7 can be rationalized as shown in Scheme I. Proton transfer could convert the 2-lithio species 6d into the 5-lithio species 8. Loss of the elements of telluroformaldehyde and tellurium metal would give lithium phenylacetylide, which could then capture TMSCl to give 7. Upon warming, TMSCl and 5d did not give readily characterized products.

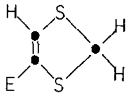
Scheme I



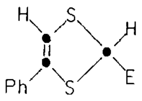
The use of alkoxide bases with 2b gave quite different results. Hydrogen-deuterium exchange in 2b was followed by ^1H NMR using 1 M $NaOCH_3$ in 1/1 (v/v) CH_3OD tetrahydrofuran-d_8 or 1 M KO-*tert*-Bu in 1/1 (v/v) *tert*-BuOD/tetrahydrofuran-d_8 at 50°C. In each base-solvent combination, deuterium was introduced at the 5-position 50 to 100 times more rapidly than at the 2-position, with essentially complete exchange at the 5-position after 1.5 h. Complete hydrogen-deuterium exchange at the 2- and 5-positions was observed after 1 week at 50°C. Ditellurole 2a was unstable to these conditions.

These results suggest that the phenyl group in the 4-position of the 1,3-ditellurole ring sterically shields the 5-position. With the strong and hindered base LDA in THF, the protons in the 2-position are easily removed to give the 2-lithiated product 6d of kinetic control. In the absence of this substituent, the thermodynamically preferred vinyl anion 5d is formed. The instability of the vinyl lithiated species in THF at high temperatures precludes the direct detection of 9 from 6d. With weaker bases ($NaOCH_3$ or KO-tert-Bu) in protic solvents, preferential formation of the vinyl anion (thermodynamically favored) from 2b is observed even with a phenyl substituent at the 4-position.[11]

The related compounds 1,3-dithiole (9a) and 4-phenyl-1,3-dithiole (10a) show similar behavior with LDA in THF. Thus, at -70°C, 9a gives 9b exclusively when treated first with LDA and then CH_3OD. On the other hand, 10a gives 10b and 10c when treated with LDA and then either CH_3OD or CH_3I, respectively.



9a, E = H
b, E = D



10a, E = H
b, E = D
c, E = CH_3

References and Notes

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10. All compounds gave satisfactory ^{1}H NMR, IR, and mass spectral data. ^{1}H NMR data: For **5a** ($CDCl_3$): δ 8.90 (s, 1 H), 4.75 (s, 2 H). For **5b** (m.p. 78.5-80.5 $CDCl_3$): δ 8.23 (d, 1 H, *J* = 1.3 Hz), 7.50 (m, 2 H), 7.33 (m, 3 H), 5.20 (d, 1 H, *J* = 1.3 Hz), 4.41 (s, 2 H). For **5c** (m.p. 53-56°C, $CDCl_3$): δ 8.07 (q, 1 H, *J* = 1.2 Hz), 4.73 (s, 2 H), 2.23 (d, 3 H, *J* = 1.2 Hz). For **6a** ($CDCl_3$): δ 8.58 (s, 1 H), 7.25 (m, 5 H), 4.72 (t, 1 H, *J* = 0.8 Hz). For **6b** ($CDCl_3$): δ 8.60 (s, 1 H), 7.30 (m, 10 H), 5.78 (d, 1 H, *J* = 8.5 Hz), 5.08 (d, 1 H, *J* = 8.5 Hz). For **6c** ($CDCl_3$): δ 8.75 (s, 1 H), 7.30 (m, 5 H), 5.12 (q, 1 H, *J* = 7.5 Hz), 2.67 (d, 3 H, *J* = 7.5 Hz). For **7** ($CDCl_3$): δ 7.40 (m, 2 H), 7.25 (m, 3 H), 0.27 (s, 9 H). For **9a** ($CDCl_3$): δ 6.08 (s, 2 H), 4.50 (s, 2 H). For **9b** ($CDCl_3$): δ 6.07 (s, 1 H), 4.50 (s, 2 H). For **10a** ($CDCl_3$): δ 7.40 (m, 5 H), 6.33 (s, 1 H), 4.57 (s, 2 H). For **10b** ($CDCl_3$): δ 7.40 (m, 5 H), 6.33 (s, 1 H), 4.55 (t, 1 H, *J* = 0.8 Hz). For **10c** ($CDCl_3$): δ 7.3 (m, 5 H), 6.30 (s, 1 H), 4.80 (q, 1 H, *J* = 6 Hz), 1.63 (d, 3 H, *J* = 6 Hz).

11. The possibility of an addition-elimination mechanism to give deuterium incorporation at the 5-position cannot be excluded with these bases. However, one would expect the addition of *tert*-butoxide anion to be much slower than addition of methoxide anion. The observed rate with potassium *tert*-butoxide was actually somewhat faster than with sodium methoxide. These data are consistent with the idea of vinyl anion formation.

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