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A SEARCH FOR SINGLE-ELECTRON TRANSFER (SET) MECHANISMS IN THE REACTION OF 1,3-DITHIANYL- AND 1,3-OXATHIANYLLITHIUMS WITH PRIMARY HALIDES

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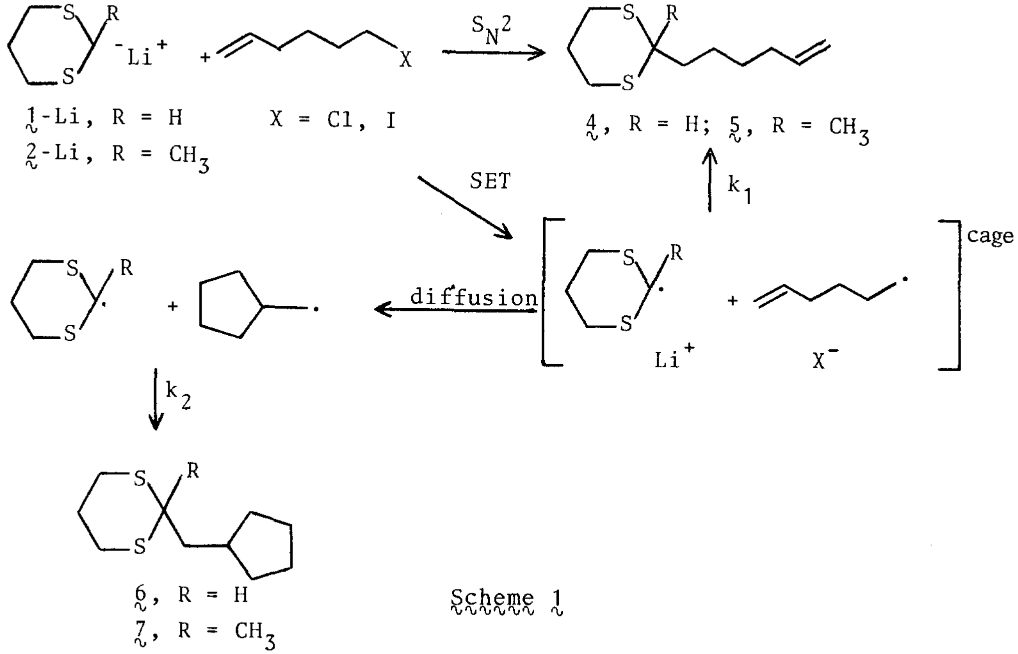
Abstract. The reaction of 1,3-dithianyl-, 2-methyl-1,3-dithianyl- and 1,3-oxathianyllithium with 6-halo-1-hexenes affords the products expected from a S_N2 (rather than SET) mechanism.

Introduction. The elegant experiments that demonstrated the importance of single-electron transfer (SET) mechanisms in the Grignard[1] and organocuprate[2] reactions have stimulated the search for related electron-transfer mechanistic pathways in many other organic reactions.[3] In view of the widespread use of dithianyllithiums in synthetic chemistry,[4] we were encouraged to examine the possible involvement of radical intermediates in the reactions of these and similar organometallics with electrophiles. The very recent report of Chung and Dunn addressing this question for 1,3-dithianyllithium[5] prompts us to communicate our findings on the reactions of the lithium salts of 1,3-dithiane (1), 2-methyl-1,3-dithiane (2) and 6,6-dimethyl-1,3-oxathiane (3) with 6-halo-1-hexenes. These primary halides are well known radical probes that are capable of producing rearranged products if radical intermediates are generated in the reaction.[6]

Results and Discussion. Treatment of 1,3-dithiane (1) with one equivalent of n-BuLi in tetrahydrofuran (THF) at -20°C gives 1,3-dithianyllithium (1-Li) in quantitative yield. Reaction of 1-Li with either 6-chloro- or 6-iodo-1-hexene affords 2-(5-hexenyl)-1,3-dithiane as the sole product (88-92% ^{1}H NMR or VPC yield). The absence of cyclized product in reactions of **1**-Li with the chloride or iodide is in accord with the reported failure to observe SET in similar reactions of **1**-Li.[5] These results are consistent with a simple S_N2 mechanism for the alkylation of **1**-Li with primary halides.

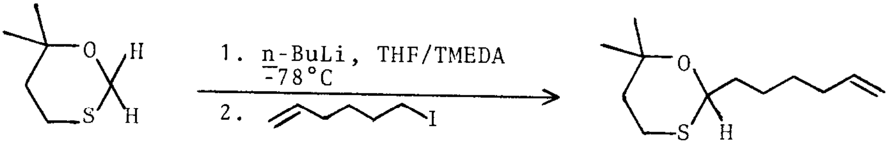


Scheme 1

The effect of alkyl substitution at C(2) on the reactions of dithianyllithium with halides was probed in experiments using 2-lithio-2-methyl-1,3-dithane (**2**). At least two factors are expected to facilitate electron transfer from **2**-Li relative to **1**-Li: first, the pK_a of **2** is *ca.* 7 units higher than that for **1**,[7] and as a consequence the oxidation potential for the former should be significantly lower;[8] and second, the derived radical **2**• will be more stable than **1**•, thus increasing the probabilities for diffusion from the solvent cage and therefore the value of k_2 relative to k_1 (Scheme 1).

In the event, alkylation of **2**-Li in THF-TMEDA at -20°C with either 6-chloro- or 6-iodo-1-hexene gave **5** (57% isolated yield from **2**) with no evidence of any cyclized products. The absence of **7** (Scheme 1) in these reactions is again consistent with a S_N2 process.

Similar behavior was observed in reactions of the oxathianyllithium derived from **3**. Incorporation of an oxygen in the six-membered ring raises the pK_a of H(2) in **3** to about 38[9] and presumably results in concomitant lowering of the ionization potential of **3**-Li.[8] As indicated in Scheme 2, no cyclized material was detected when **3**-Li was treated with 6-iodo-1-hexene.[11]



3

Scheme 2

8, 66% (VPC)

Attempts to metallate 2,6,6-trimethyl-1,3-oxathiane, whose pK_a can be estimated at *ca.* 46, with n-BuLi, t-BuLi or Lochmann's base[12] were unsuccessful.

Conclusion. The present observations seem to rule out the involvement of SET mechanisms in the reaction of 2-lithio-1,3-dithiane, its 2-methyl derivative and 1,3-oxathianyllithium with primary halides, at least in weakly polar solvents[13] (THF, THF/TMEDA) and at low temperatures (-20°C, -78°C).

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9. Professor Bordwell has measured the following carbon acidity values in DMSO: $C_6H_5SO_2\underline{CH_2}SCH_3$, pK_a = 23.4; $C_6H_5SO_2\underline{CH_2}OCH_3$ = 30.7.[10] Since the pK_a for 1,3-dithianes is 31.1,[7] we estimate that the pK_a for 1,3-oxathiane is close to 38.4.
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11. The methyl groups in **3** are needed to prevent Wittig-type rearrangements in the derived carbanion: Koskimies, J.K., *Ph.D. Thesis*, University of North Carolina at Chapel Hill, 1976.
12. *cf.*Bates, R.B.; Hess, B.A.; Ogle, C.A.; Schaad, L.J., *J. Am. Chem. Soc.*, 1981, **103**, 5052-5058.
13. There are contrasting expectations for solvent effects: Professor Kuivila[14] has suggested that the electron-transfer mechanism competes more effectively with the S_N2 mechanism in less efective cation--solvating media. On the other hand, Chung and Dunn[5] anticipate HOMO-raising perturbations from the solvation of the cation, thus facilitating electron donation.
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