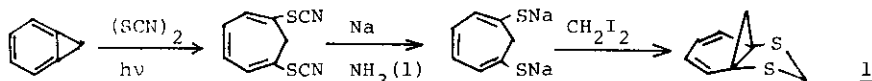


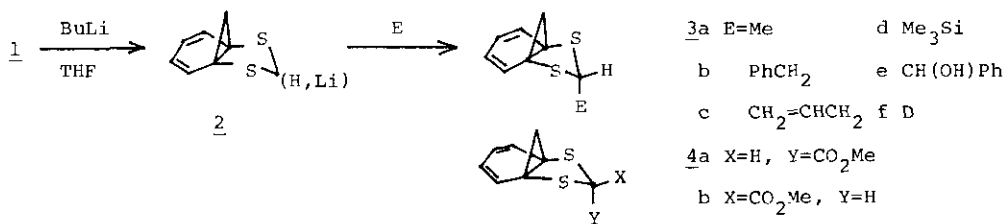
REACTIVITY OF CARBANIONS ADJACENT TO SULFUR ATOM IN SULFUR HETEROCYCLES

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Dithiatricyclodecadiene (1) was prepared by the following route.



On treatment with butyllithium in THF at -78 °C, 1 was converted to anion (2), which reacted with various electrophiles (alkyl halides, silyl halide, carbonyl compounds, and D₂O) to afford 8-substituted products (3 and 4).



Within the limit of detection by NMR spectroscopy, there was found only one isomer for all the products (3), suggesting the endo selectivity is at least more than 20. That the product has an endo structure was established by NMR spectroscopy using long-range coupling and lanthanide induced shift for 4.

Whether the endo selectivity results from kinetic or thermodynamic control was determined using deuterated compounds (5 and 6), and $k_{\text{endo}}/k_{\text{exo}}=9.0$ and $k_{\text{H}}/k_{\text{D}}=2.8$ were obtained. This suggests that the endo selectivity comes from thermodynamic control. This endo selectivity is interesting in view of the reported equatorial selectivity of related 1,3-dithiane system (7). The reason for the selectivity of the present system is also discussed.

