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STEREOSPECIFIC CYCLISATIONS OF SUBSTITUTED α'-LITHIATED α(Z),Y-BUTADIENYL SULFOXIDES

Marius Reglier * and Sylvestre A. Julia

E.R.12 du C.N.R.S., Laboratoire de Chimie, Ecole Normale Supérieure,
24 rue Lhomond, 75231 Paris Cedex 05, France

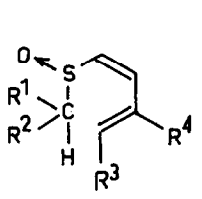
Summary. The title compounds 2(b-d) were prepared and converted stereospecifically to the lithiated derivatives of cyclic sulfoxides 3(b-d) through a proposed concerted disrotatory electrocyclisation.

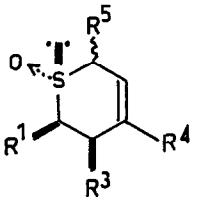
Two previous communications have described the cyclisation of several substituted α'-lithiated α(Z),Y-butadienyl sulfides to lithio-thiacyclohexenes which in turn undergo several different rearrangements [1,2].

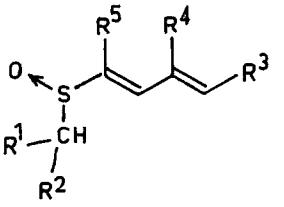
The known stability of α-lithio-sulfoxides has led us to investigate the properties of α'-lithiated α(Z),Y-butadienyl sulfoxides. The substrates 1(a-d) were easily obtained through mild oxidation (m.chloroperoxybenzoic acid, CH_2Cl_2, -78°C to +15°C) of the previously described (Z)-dienic sulfides [1-3] (yields of purified sulfoxides were 69, 55, 63 and 66 % respectively).

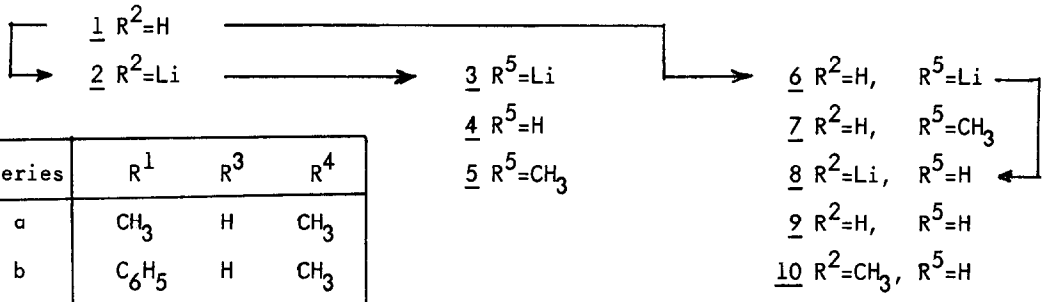
When the sulfoxide 1a was treated with a slight excess of lithium diisopropylamide (LDA) at -78°C then with methyl iodide, the α-methylated product 7a was obtained (table 1, entry 2) [4]. The latter compound is probably the (E)-isomer, since protonation of the intermediate anion 6a gave the (E)-dienic sulfoxide 9a (entry 1) [5].

The other sulfoxides 1(b-d) bearing benzylic or allylic moieties adjacent to sulfur underwent selective deprotonation at this site, followed by cyclisation to afford, after quenching with H_2O, the cyclic sulfoxides 4 (or 5 when the quenching agent is CH_3I) as the major product, contaminated by a small amount of the (E)-dienic sulfoxides 9 (or 10). It is presumed that the latter products arise from partial lithiation at the α-vinylic position of the starting (Z)-dienic sulfoxide 1 followed by a rapid (Z) to (E) isomerisation affording the (E)-vinylic anion, as was found with the sulfoxide 1a. Finally a [1.3] prototropic shift affords the anions 8 which, after addition of water or CH_3I, give the products 9 and 10 respectively. More noteworthy is that all formed cyclic sulfoxides 4 are pure isomers with stereochemistry shown in the formulas 4(b-d).









Series	R^1	R^3	R^4
a	CH_3	H	CH_3
b	C_6H_5	H	CH_3
c	$(CH_3)_2C{=}CH$	H	CH_3
d	C_6H_5	$-(CH_2)_4-$	

Table 1

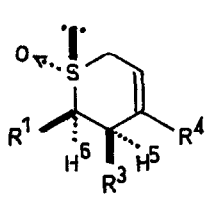
Entry	Substrate	Conditions	Quenching Reagent	Products (yields %)*
1	1a	i; 30 min at -78°C	H_2O	9a (68)
2	1a	idem	CH_3I	7a (50)
3	1b	i; 2 h at -78°C	H_2O	4b (55); 9b (18)
4	1b	i; warming to -30°C then 2 h at -30°C	H_2O	4b (56); 9b (18)
5	1b	idem	CH_3I	5b (46) [55/45] 10b (17) [18/82]
6	1c	i; warming to -30°C then 2 h at -30°C	H_2O	4c (44); 9c (17.5)
7	1c	idem	CH_3I	5c (32) [63/47] 10c (18) [43/57]
8	1c	ii; warming to -30°C then 2 h at -30°C	H_2O	4c (44); 9c (18)
9	1d	i; warming to -30°C then 2 h at -30°C	H_2O	4d (68); 9d (15)

* [ratios] of isomers

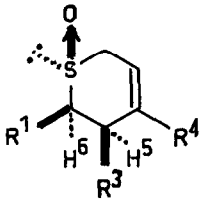
i 1.2 equiv of LDA was added to a cooled (-78°C) solution of the substrate in THF

ii same as i, but with CH_3Li instead of LDA.

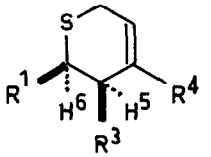
In order to elucidate the stereochemistry of the products 4(b-d) obtained from these cyclisations, the sulfides 12, sulfoxides 11 and sulfones 13 were prepared and characterised by ^{1}H-NMR. By comparison of the spectra of these compounds with those of sulfoxides 4(b-d) as well as the effects of solvent (benzene) and europium salts on the chemical shifts of sulfoxides 4 and 11 [6], we were able to establish the trans orientation of the sulfoxide group and R^1 for compounds 4(b-d). For sulfoxides 4d, 11d, sulfide 12d and sulfone 13d the coupling constants between H^6 and H^5 were 5.5, 6, 4.5 and 6 Hz respectively; this indicate a cis orientation of the groups R^1 and R^3 [7].



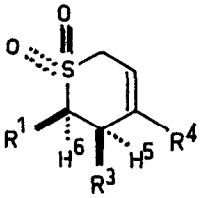
4(b-d)



11(b-d)



12(b-d)

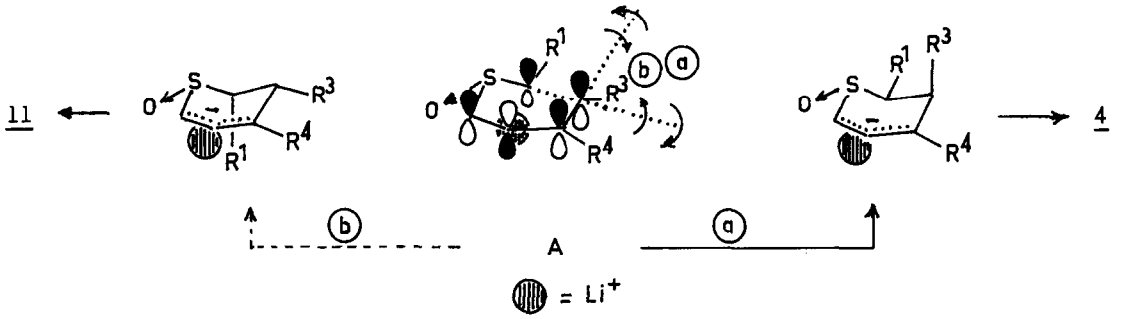


13(b-d)

Table 2

Substrate	Conditions	Yields (%)	Products (ratios)
4c	P_4S_{10}; CH_2Cl_2 [8]	63	12c
4d	idem	66	12d
12b	1 equiv m.CPBA, CH_2Cl_2; -78°C to +15°C	71	4b (60); 11b (40)
12d	idem	70	4d
4b	$(C_2H_5)_3O^{\oplus}BF_4^{\ominus}$, CH_2Cl_2, then NaOH [9]	50	11b
4d	idem	45	11d
4b	1 equiv m.CPBA, CH_2Cl_2; -78°C to +15°C	82	13b
4c	idem	86	13c
4d	idem	85	13d

The stereospecific formation of sulfoxides 4(b-d) can be explained by a concerted disrotatory electrocyclisation [10] of the intermediate A in which the lithium is chelated to the anionised carbon, oxygen and dienic system [11]. It is clear that, due to steric factors, process (a) which leads to 4 is more facile than process (b) which would afford 11. During process (b), the groups R^1 and R^3 encounter steric hindrance with the lithium atom whereas in process (a) this interaction is avoided.



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