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ON THE PROPERTIES OF SOME SUBSTITUTED α'-LITHIATED α(Z),γ-BUTADIENYL SULFIDES: CYCLISATIONS AND REARRANGEMENTS

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Summary. The conditions for the preparation and cyclisation of the title compounds 3 are described. The stability of the intermediate lithio-thiacyclohexenes 4 is shown to depend on the reaction conditions and the substituents R^1-R^4. The final products 6, 10 and 7 arise from 4 via a [1.4] sigmatropic rearrangement, a [1.3] prototropic shift followed by a [2.3] sigmatropic rearrangement, or the elimination of lithium methanethiolate respectively.

We recently reported the stereoselective conversion of lithiated benzylic 3-methyl-1(Z),3-butadienyl sulfide 3a (R^2=H) into the cis-disubstituted cyclopropane 5a [1]. In order to verify that this product 5a arises from the lithiated thiacyclohexene 4a (R^2=H) by a [1.4] sigmatropic rearrangement [2], we studied the metalation of thiacyclohexene 2a (R^2=R^5=H). Entry 1 shows that under certain conditions, the carbanion 4a (R^2=H) can be trapped with methyl iodide. When this carbanion 4a (R^2=H) was submitted to the same conditions as for 3a (R^2=H)(HMPA/-30°C/CH_3I), the same cyclopropane compound 6 was obtained as major product but with a small amount of another cyclopropane compound 10a (entry 6).

When the thiacyclohexene 2a (R^2=R^5=H) was present in excess relative to the base, the new cyclopropane compound 10a [3] was obtained as the sole product with an equal amount of the starting material (entry 11). Likewise, when the sulfide 1a (R^2=H) was present in excess relative to the base, the same cyclopropane compound 10a was obtained with an equal amount of the thiacyclohexene 2a (R^2=R^5=H) (entry 10). These results can be explained by intermolecular proton shifts [4]. As soon as it is formed, the thiacyclohexene lithio-derivative 4a (R^2=H) can be protonated:

- by the starting material 1a (R^2=H) to give the benzylic carbanion 3a (R^2=H) which cyclises to 4a (R^2=H) and the cycle repeats;
- by the thiacyclohexene 2a (R^2=R^5=H) when the dienic sulfide is absent or consumed; this new thiacyclohexene lithio-derivative 8a can then undergo a classical [2.3] sigmatropic rearrangement to give 9a, the precursor of the cyclopropane compound 10a.

Table

Entry	Substrate	Conditions	yield % *	Products (proportions)
1	2a R^2=R^5=H	ii; quenching at -78°C with CH_3I	90	2a (R^2=H, R^5=CH_3) (t/c = 75/25)
2	1b R^2=H	i; idem	80	1b (R^2=CH_3)
3	1c R^2=H	i; warming to -30°C then 2 h at -30°C and quenching with CH_3I	(99)	1c (R^2=CH_3)
4	1b R^2=H	i; warming to -30°C then 2 h at -30°C and quenching with H_2O	60	2 b (R^5=H) (t/c = 75/25)
5	1b R^2=H	idem, quenching with CH_3I	62	2b (R^5=CH_3) (three isomers 64/18/18)
6	2a R^2=R^5=H	ii; 1.2 equiv HMPA added, warming to -30°C then 2 h at -30°C and quenching with CH_3I	90	6 (78); 10a (22)
7	1b R^2=H	i; idem	51	2b (R^2=H, R^5=CH_3) (15); 10b (85)
8	1c R^2=H	iii; idem	71	10c
9	1c R^2=H	iv; quenching with H_2O	46	7
10	1a R^2=H	v; 1.2 equiv HMPA added, warming to -30°C then 2 h at -30°C and quenching with CH_3I	(93)	2a (R^2=R^5=H) (50); 10a (50)
11	2a R^2=R^5=H	vi; idem	(95)	2a (R^2=R^5=H) (50); 10a (50)
12	1c R^2=H	v; idem	(98)	2c (R^2=R^5=H) (50); 10c (50)

* The numbers in brackets are the yields of crude products.

i 1.2 equiv of n.C_4H_9Li was added to a cooled (-78°C) solution of the substrate in THF and the mixture stirred at that temperature for 30 min.

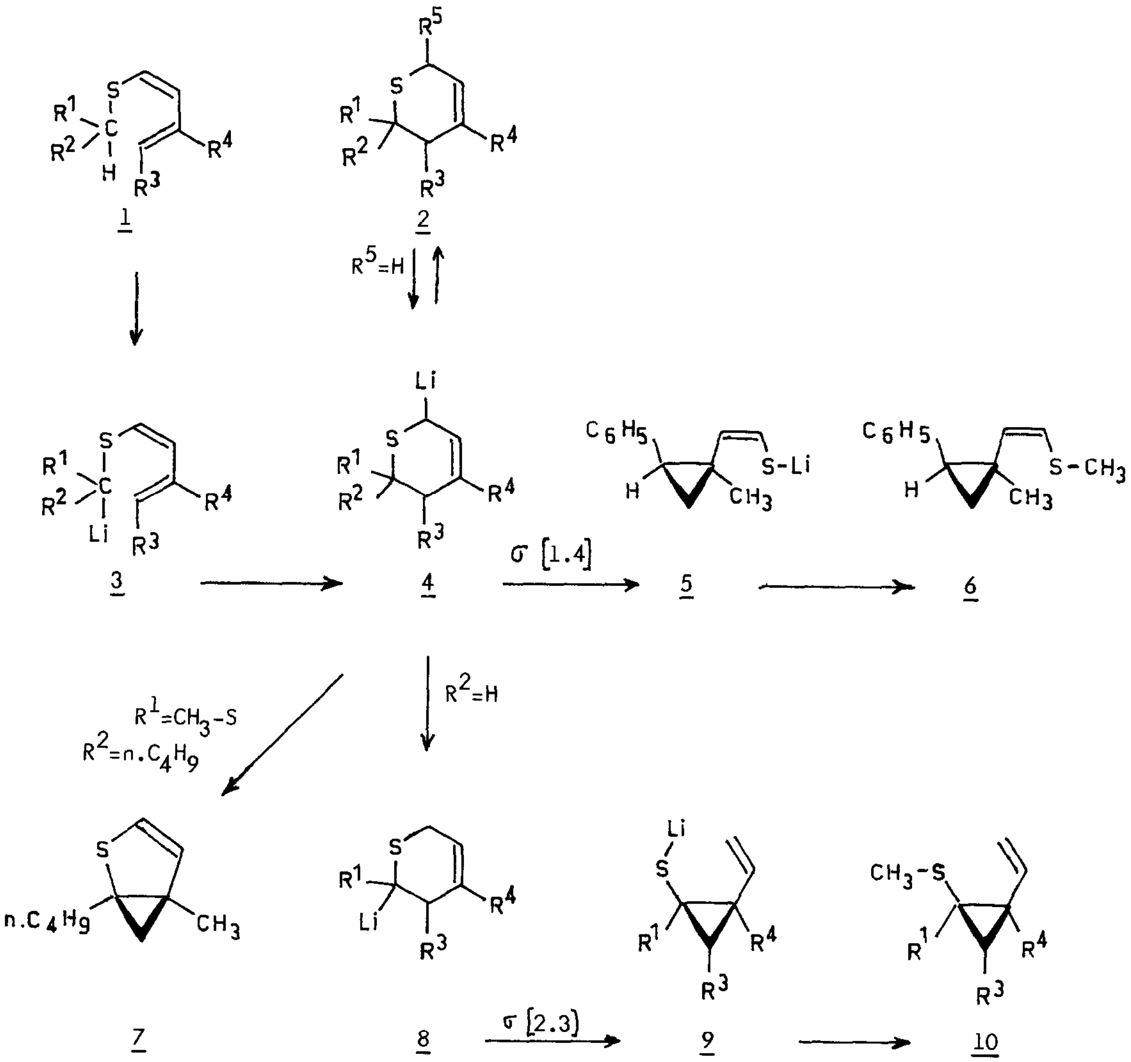
ii same as i, but with sec.C_4H_9Li instead of n.C_4H_9Li.

iii same as i, but with lithium diisopropylamide (LDA) instead of n. C_4H_9Li.

iv same as i followed by addition of 1.2 equiv of n.C_4H_9I and warming to 18°C; then at -78°C, 1.2 equiv of n.C_4H_9Li added, 30 min; then 1.2 equiv HMPA added, warming to -30°C and 2 h at -30°C.

v same as i, but 0.5 equiv of n.C_4H_9Li instead of 1.2 equiv.

vi same as ii, but with 0.5 equiv of sec.C_4H_9Li instead of 1.2 equiv.



Series	R^1	R^2	R^3	R^4	R^5
a	C_6H_5	H or CH_3	H	CH_3	H or CH_3
b	C_6H_5	H	-$(CH_2)_4$-		H or CH_3
c	CH_3-S	H or CH_3 or n.C_4H_9	H	CH_3	-

Two new cyclopropane compounds 10b,c were obtained by cyclisation and rearrangement of (Z)-dienyl sulfides 1b (R^2=H) and 1c (R^2=H) respectively. These (Z)-dienyl sulfides were prepared in yields of 70 and 48 % by the nucleophilic addition of thiol to the enyne under basic conditions [5].

At -30°C, the lithiated sulfide 3b (R^2=H) underwent smooth cyclisation to the stable lithiated thiacyclohexene 4b (trans/cis = 75/25)(entries 4, 5); however, when 3b was treated with 1.2 equiv of HMPA at the same temperature and quenched with methyl iodide, it did not give the product of a [1.4] sigmatropic rearrangement, but afforded the cyclopropane compound 10b as the major product (entry 7).

Finally, the isoprenic dithioacetal 1c (R^2=H) afforded three different products depending on the reaction conditions:

- when treated with a slight excess of LDA and HMPA, then with methyl iodide, it was smoothly converted into the cyclopropanone dithioacetal 10c (entry 8) [6];
- when 1c (R^2=H) was present in excess relative to the base, it yielded analogous to 1a (R^2=H), a mixture of the thia-cyclohexene 2c (R^2=R^5=H) and the cyclopropane 10c (entry 12);
- and when treated with a slight excess of n.butyllithium followed by n.butyl iodide and then again with n.butyllithium and HMPA, it gave a lithio-thiacyclohexene 4c (R^2=n.C_4H_9) which, unable to undergo the aforementioned proton shift leading to vinylcyclopropane 10, suffers loss of lithium methanethiolate [7] to afford 7 as the sole product (entry 9).

A full account of this work including additional examples and a detailed mechanistic analysis will be published elsewhere.

REFERENCES AND NOTES

1. M. Reglier, S.A. Julia, Tetrahedron Letters, 1983, 24, 2387.
2. J.F. Biellmann, J.B. Ducep, J.J. Vicens, Tetrahedron, 1976, 32, 1801.
3. All new compounds exhibited the expected IR, N.M.R. (^{1}H, ^{13}C) and mass spectral properties.
4. As it was reported for the lithiation of allyl benzyl sulfide: J.F. Biellmann, J.B. Ducep, D. Schirlin, Tetrahedron, 1980, 36, 1249.
5. R.H. Everhardus, R. Gräfing, L. Brandsma, Synthesis, 1983, 623; M. Reglier, O. Ruel, R. Lorne, S.A. Julia, ibidem, 1983, 624.
6. The compound 10c is analogous to those obtained by [2.3] sigmatropic rearrangement of appropriate sulfonium ylides: E.J. Corey, S.W. Walinsky, J. Amer. Chem. Soc., 1972, 94, 8932.
7. A similar ring closure to a cyclopropane compound due to an intramolecular displacement of phenylthiolate ion by an allylic aliphatic lithio-derivative has been reported: O. Ruel, B. Cazes, S. Julia, Synthetic Commun., 1980, 10, 743.

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