Journal of Organometallic Chemistry, 302 (1986) 1–4
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ON THE STEREOCHEMICAL STABILITY OF α-SULFONYLVINYLLITHIUM COMPOUNDS

H. KLEIJN and P. VERMEER*

Department of Organic Chemistry, State University at Utrecht, Croesestraat 79, 3502 JB Utrecht (The Netherlands)

(Received August 19th, 1985)

Summary

α-Lithiated vinylic sulfones have been prepared from readily available 1-alkenyl sulfones in tetrahydrofuran by treatment with methyllithium at −90°C; they appear to be configurationally unstable at −60°C.

Introduction

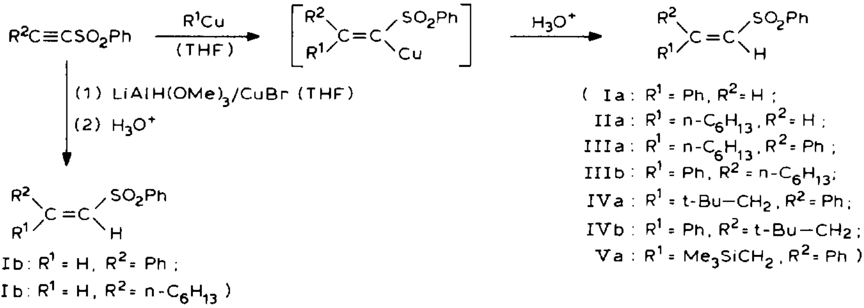
1-Alkenyl sulfones are reagents of synthetic interest. They can be used, for instance, to construct carbocycles [1,2] and as dienophiles in Diels–Alder reactions [3,4]. Reduction of the compounds with sodium dithionite [5] or aluminium amalgam [6] gives olefins stereospecifically, whilst reaction with organometallic reagents in the presence of transition metal complexes results in replacement of the sulfonyl group, by e.g. alkyl [7].

It is clear that α-lithiated vinylic sulfones could be useful building blocks in organic synthesis, for instance in preparing insect pheromones in which stereochemically pure double bonds are present. In the literature there are two examples of α-lithiation and subsequent derivative formation with retention of configuration [8]. In this connection it was of interest to know whether such configurational stability is a general feature of α-lithiated sulfones, since their synthetic merits will be closely related to stereochemical stability. In this paper we present the results of a study in this field.

Results and discussion

For our study we first prepared a number of *E*- and *Z*-1-alkenyl sulfones (I–V) in yields over 90% by reaction of appropriate 1-alkynyl sulfones with organocopper reagents [9] and by reduction of some 1-alkynyl sulfones with "copper hydride" following the procedure we reported for the reduction of 1-alkynyl sulfides [10] (Scheme 1).

0022-328X/86/$03.50



SCHEME 1

The fact that I–V were stereochemically (nearly) pure shows that the intermediary α-cupriovinylic sulfones are configurationally fairly stable under the conditions of their formation (see refs. 9 and 10). To tetrahydrofuran solutions of the 1-alkenyl sulfones I–V thus obtained was then added a solution of methyllithium in Et_2O (the methyllithium solution was obtained from lithium metal and methyl iodide and therefore contained lithium iodide) at −90°C as previously described [8]. The temperature of the resulting α-lithiovinylic sulfone solution was then raised to −60°C, the mixture stirred at that temperature for the period indicated in Table 1, and then poured into saturated aqueous ammonium chloride. The sulfone composition was then analysed by means of ^{1}H NMR spectroscopy.

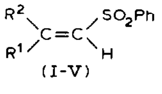
From the data listed in Table 1 it is evident that in every case more or less *E/Z* isomerisation of the α-lithiovinylic sulfones occurred:

$$\underset{\text{(Ia–Va)}}{R^1R^2C{=}CHSO_2Ph} \underset{H_2O}{\overset{MeLi}{\rightleftharpoons}} [R^1R^2C{=}C(Li)SO_2Ph] \underset{MeLi}{\overset{H_2O}{\rightleftharpoons}} \underset{\text{(Ib–Vb)}}{R^1R^2C{=}CHSO_2Ph}$$

The results can be explained by assuming that steric factors control the isomerisations. Thus lithiated sulfone Ia is nearly configurationally stable as the two groups

TABLE 1

REACTION CONDITIONS FOR THE EQUILIBRATION OF *E*- AND *Z*-$R^1R^2C{=}CHSO_2Ph$ (I–V) [a]

Entry	Starting compound		 (I-V)	Reaction time [b] (h)	Product composition [c]
	R^1	R^2			
1	Ph	H	Ia	1.0	Ia/Ib: 97/3
2	H	Ph	Ib	1.0	Ia/Ib: 97/3
3	n-C_6H_{13}	H	IIa	1.0	IIa/IIb: 91/9
4	H	n-C_6H_{13}	IIb	1.0	IIa/IIb: 40/60
5	H	n-C_6H_{13}	IIb	8.0	IIa/IIb: 85/15
6	n-C_6H_{13}	Ph	IIIa	1.5	IIIa/IIIb: 25/75
7	Ph	n-C_6H_{13}	IIIb	1.5	IIIa/IIIb: 25/75
8	t-BuCH_2	Ph	IVa	1.5	IVa/IVb: 32/68
9	Ph	t-BuCH_2	IVb	1.5	IVa/IVb: 30/70
10	Me_3SiCH_2	Ph	Va	1.0	Va/Vb: 6/94

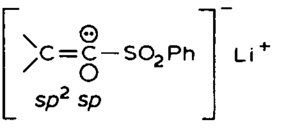
[a] Solvent: THF/Et_2O (1/1 v/v); see the experimental section for concentrations. [b] Reaction temperature −60°C. [c] Determined by means of ^{1}H NMR spectroscopy.

Ph (= R^1) and SO_2Ph strongly prefer the *trans* orientation (entry 1); the α-lithio derivative of its geometric isomer Ib rapidly isomerises into that of Ia (entry 2). The equilibrium mixture in this case consists of 97% of the α-lithio derivative of Ia and 3% of that of Ib. A comparable result was found for the α-lithio derivatives of IIa and IIb (see entries 3–5 in Table 1) where a *trans* orientation of the n-hexyl group and the SO_2Ph function is most favourable.

From entry 10 it can be seen that steric interaction between the SO_2Ph group and the group Me_3SiCH_2 is much less than that between the former and the phenyl group. The product ratio, viz. 6/94, probably reflects the equilibrium composition, but we have not confirmed that by taking the geometric isomer of Va, since it was not available. Longer reaction times did not measurably change the ratio Va/Vb, however.

Entries 6 and 7 reveal that steric hindrance between the group SO_2Ph and a phenyl group is more pronounced than that between the group SO_2Ph and the n-hexyl group. A comparable result was obtained in the case of a neopentyl group and a phenyl group (entries 8 and 9). It is noteworthy that a neopentyl group exerts more steric hindrance than a Me_3SiCH_2 group.

The isomerisations proceeded relatively fast. Generally equilibrium was reached at −60°C within 1.0–1.5 h. However, the isomerisation slowed down when no phenyl group was present on the β-carbon atom (compare entries 3–5 with the other ones). The accelerating influence of a phenyl group may be due to a lowering of the bond order of the isomerising double bond by conjugation with the phenyl group. The exact mechanism of the isomerisation is not clear at the moment; one could envisage a mechanism in which the isomerisation proceeds through linear species of the following type:



Conclusion

From the results it is evident that the configurational stability of α-lithiovinylic sulfones is low, even at −60°C. Consequently, their value as building blocks for construction of isomerically pure olefins is restricted, especially because derivatisation of vinylic sulfones by reaction of their α-lithio derivatives with electrophiles generally requires temperatures above −60°C.

Experimental section

All reactions were performed under dry nitrogen. The required 1-alkenyl sulfones were obtained as described in refs. 9 and 10. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ before use. Methyllithium was obtained as a solution in Et_2O by treating lithium metal with methyl iodide in this solvent; its molarity was determined by Watson's titration method [11].

^1H NMR spectra were recorded with a Varian EM-390 spectrometer for $CDCl_3$ solutions using Me_4Si as internal standard.

General procedure for the lithiation of I–V

A solution of methyllithium (0.005 mol) in Et_2O (15 ml) was added dropwise, at −90°C, to a stirred solution of sulfone I–V (0.005 mol) in THF (15 ml). The temperature of the mixture was then allowed to rise to −60°C during 5 min and the mixture was stirred for the period indicated in Table 1. It was then poured into saturated aqueous NH_4Cl (100 ml). The sulfones were isolated by extraction with CH_2Cl_2 (3 × 30 ml). The combined extracts were washed with water and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue analysed by ^1H NMR spectroscopy. In all cases there was sufficient difference in the δ-values of the double bond proton(s) to permit reliable estimates of the product composition. The following ^1H NMR data are characteristic for the compounds (δ-values are given in ppm; positive values are positions downfield from Me_4Si; the double bond protons indicated all belong to the isomerising double bond). Ia: 7.60 (d, =CH, *J* 15.8 Hz), 6.86 (d, =CH, *J* 15.8 Hz); Ib: 6.97 (d, =CH, *J* 12.5 Hz), 6.40 (d, =CH, *J* 12.5 Hz); IIa: 6.90 (dt, =CH, *J* 6.4, 14.9 Hz), 6.25 (d, =CH, *J* 14.9 Hz), 2.20 (m, CH_2C=); IIb: 6.10–6.40 (m, 2 × =CH), 2.64 (m, CH_2C=); IIIa: 6.42 (s, =CH), 2.32 (t, CH_2C=); IIIb: 6.32 (s, =CH), 3.02 (t, CH_2C=); IVa: 6.42 (s, =CH), 2.33 (s, CH_2C=), 0.80 (s, t-C_4H_9); IVb: 6.22 (s, =CH), 3.13 (s, CH_2C=), 0.88 (s, t-C_4H_9); Va: 6.38 (s, =CH), 2.05 (s, CH_2C=), −0.01 (s, Me_3Si); Vb: 6.16 (s, =CH), 2.77 (s, CH_2C=), 0.08 (s, Me_3Si).

References

1 J.J. Eisch and J.E. Galle, J. Org. Chem., 44 (1979) 3277.
2 R.V.C. Carr and L.A. Paquette, J. Am. Chem. Soc., 102 (1980) 853.
3 R.V.C. Carr, R.V. Williams and L.A. Paquette, J. Org. Chem., 48 (1983) 4976.
4 W.A. Kinney, G.D. Crouse and L.A. Paquette, J. Org. Chem., 48 (1983) 4986.
5 J. Bremmer, M. Julia, M. Launay and J.P. Stacino, Tetrahedron Lett., (1982) 3265.
6 V. Pascali and A. Umani-Ronchi, J. Chem. Soc., Chem. Commun., (1973) 351.
7 J.L. Fabre, M. Julia and J.N. Verpeaux, Tetrahedron Lett., (1982) 2469.
8 J.J. Eisch and J.E. Galle, J. Org. Chem., 44 (1979) 3279.
9 J. Meijer and P. Vermeer, Recl. Trav. Chim. Pays-Bas, 94 (1975) 14.
10 P. Vermeer, J. Meijer, C. Eylander and L. Brandsma, Recl. Trav. Chim. Pays-Bas, 95 (1976) 25.
11 S.C. Watson and J.F. Eastham, J. Organomet. Chem., 9 (1967) 165.