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UNSYMMETRICAL DITHIOCARBONATE *p*-TOLUENESULFONYLHYDRAZONE: GEOMETRICALLY SELECTIVE PREPARATIONS AND DETERMINATIONS OF THE *Z*-*E* STEREOCHEMISTRY

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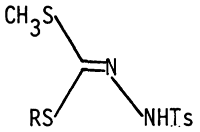
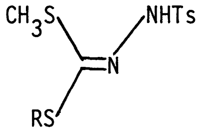
Geometrically selective preparations of each of the stereoisomers of S-alkyl (or allyl)-S'-methyl-dithiocarbonate tosylhydrazones (**1**) are described. The *Z*-*E* stereochemistry of **1** has been determined by means of equilibration experiments and NMR methods. On the basis of the geometrical assignments of **1**, the stereoselectivity in alkylations of sodium dithiocarbazates is discussed on mechanistic grounds.

Dithiocarbonate *p*-toluenesulfonylhydrazones (tosylhydrazones)[1)] have been well secured as precursors of bis(alkylthio)carbenes[2,3)] and unsymmetrical ones such as **1** possess the *Z*-*E* stereochemistry. Although the *Z*-*E* stereochemistry of ketone tosylhydrazones has been extensively studied,[4)] no studies on the geometrical isomerism of these particular tosylhydrazones (**1**) have been reported. In connection with an independent research of the stereochemistry of alkylation of dianions derived from **1**,[5)] we had needed an unequivocal method for the determination of the *Z*-*E* stereochemistry of **1**. In particular, we had been interested in the stereochemistry of allylic derivatives (**1**, R = various allylic groups), since a final goal of our research project is to investigate the [2,3]sigmatropic rearrangement of allylic dithiocarbenes.[3)] We now wish to report geometrically selective preparations of each stereoisomer of **1** and a reliable method for assigning the *Z*-*E* stereochemistry.

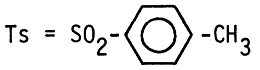


(*Z*)-**1**



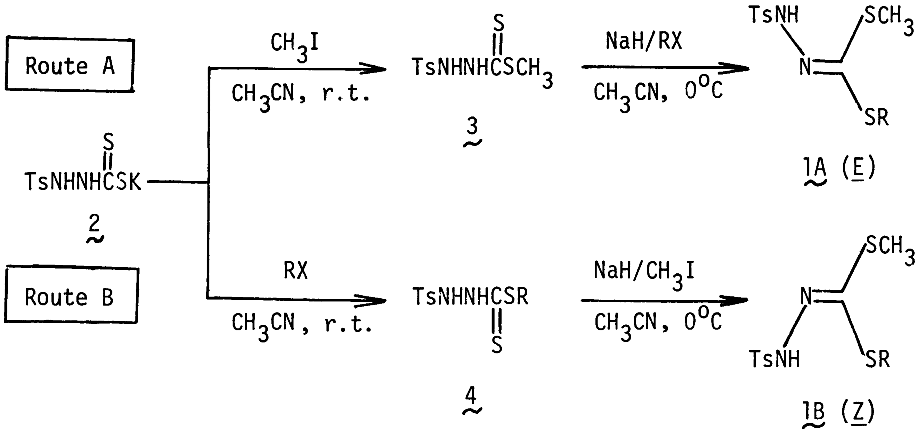
(*E*)-**1**

R ≠ CH_3



In this work, tosylhydrazones **1** were prepared via the two routes (A and B) as depicted in Scheme 1. Route A involves methylation of the potassium salt (**2**) followed by alkylation (or

Scheme 1



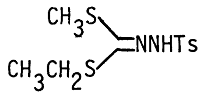
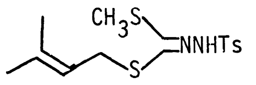
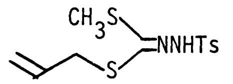
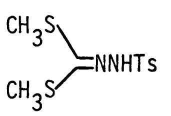
allylation) of the sodium salt of the S-methyldithiocarbazate (**3**) to provide good overall yields (>60%) of the corresponding tosylhydrazone (**1A**). These tosylhydrazones (**1A**) were found to be geometrically pure by NMR assay. On the other hand, route B involving an initial alkylation (or allylation) followed by methylation afforded the corresponding tosylhydrazone (**1B**) in good overall yields (>60%). NMR comparisons of **1A** with **1B** indicate that the stereochemistries of **1A** and **1B** are opposite each others. Some physical and spectral properties of the tosylhydrazones are summarized in Table 1.

Thus the question raised here is which stereoisomer possesses the *E* configuration. On the basis of both the result of equilibration experiments and spectral and mechanistic arguments described below, **1A** and **1B** were unequivocally assigned to the *E*- and *Z*-isomers, respectively.

First of all, relative thermal stabilities of **1A** and **1B** were examined by equilibration experiments. When each isomer was refluxed in benzene for 6 h, equilibrium was established and the ratio of **1A** vs. **1B** was determined by NMR method (Table 1). We found that the equilibrium values, K (**A**/**B**), were larger than unity and that **1B** was equilibrated more rapidly than the corresponding **1A**. These results indicate that **1A** is thermodynamically more stable than the corresponding **1B**, suggesting that the bulkier group (R) of **1A** might be situated in the position *anti* to the tosylamino moiety, that is to say, **1A** possesses the *E* configuration.

The stereochemical assignment is supported by NMR comparisons of **1A** with **1B**. As the NMR data in Table 1 show, the chemical shift of the S-methyl protons of **1A** is about 0.10 - 0.15 ppm upfield from the chemical shift of these protons of the corresponding **1B** in deuterochloroform. In view of a ring-current effect of the benzene nucleus of the tosylamino moiety, we expect that the S-methyl protons situated in the position *syn* to the tosylamino moiety might resonate at higher fields. Therefore, the stereochemistry of **1A** can be assigned to the *E* configuration in which the S-methyl group is situated in the *syn* position. Of particular interest are the observed $\Delta\delta$ values ($\Delta\delta = \delta$ in chloroform - δ in benzene) for **1A** and **1B** (see Table 1). In comparisons of $\Delta\delta$ values of **1A** with

Table 1. Physical and Spectral Data of Stereoisomers of Tosylhydrazones (**1**)

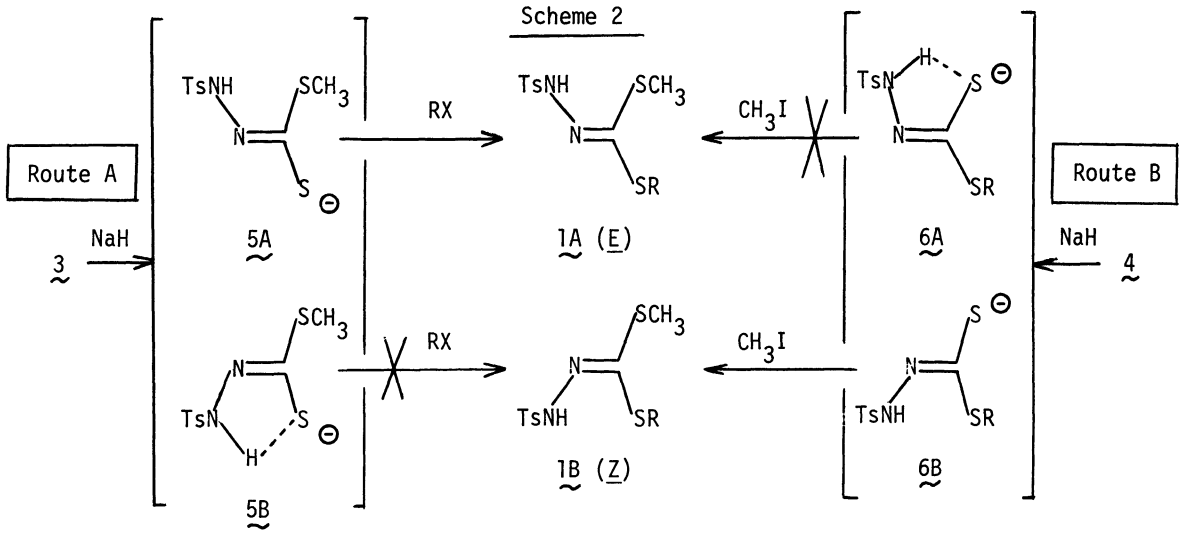
Hydrazones		A-isomer (E)			B-isomer (Z)			K(A/B)[b]
		Mp, °C	δ($CDCl_3$)ppm $-SCH_3$ (Δδ, Hz)[a]	 $-SCH_2-$	Mp, °C	δ($CDCl_3$)ppm $-SCH_3$ (Δδ , Hz)[a]	 $-SCH_2-$	
	(**1a**)	117-119	2.28 (17.4)	2.90 (33.6)	84-86	2.43 (45.0)	2.90 (16.0)	1.30 (1.38)[c]
	(**1b**)	73.5-75	2.32 (16.8)	3.53 (17.4)	100-103	2.42 (40.2)	3.53 (0.0)	1.46
	(**1c**)	107-108	2.32 (19.2)	3.53 (28.2)	96-98	2.43 (41.4)	3.53 (13.2)	1.07
					SCH_3	SCH_3		
	(**1d**)	150-151		δ ($CDCl_3$)	2.32	2.42		
				δ (benzene)	1.95	1.67		

[a] Δδ = δ ($CDCl_3$) - δ (benzene). [b] Reflux in benzene . [c] At 75 ± 1 °C .

those of **1B**, we can see a significant trend which is relevant to the stereochemical problem; benzene not only shifts the resonances of the S-methylene protons of **1A** to higher fields than does those of the corresponding **1B** but also shifts the resonances of the S-methyl protons of **1B** to higher fileds than does those of the corresponding **1A**.6) Although the exact origin of the effect of an aromatic solvent is still uncertain,7) these Δδ values appear to be widely useful for assigning the configurations of dithiocarbonate tosylhydrazones.

Finally, let us discuss the stereochemistry of alkylations (or allylations) of anions derived from the dithiocarbazates (**3** or **4**). If the geometrical assignments described above are correct, both alkylation (or allylation) of **3** for route A and methylation of **4** for route B should take place exclusively at the position anti to the tosylamino moiety as depicted in Scheme 2. This is very likely since the anti-sulfur anions (**5A** and **6B**) should be more reactive than the syn counterparts (**5B** and **6A**) for steric reasons and the nucleophilicity of the syn-sulfur anions might be lowered by the hydrogen bonding as illustrated in Scheme 2. Thus these mechanistic arguments are also consistent with the geometrical assignments described above.

Scheme 2



References and Notes

1) According to the IUPAC nomenclature, this class of compounds is referred to as 1-[bis(alkylthio)-methylene]-2-(4-methylbenzenesulfonyl)hydrazines.

2) U. Schollköpf and E. Wiskott, Justus Liebigs Ann. Chem., 694, 44 (1966); N. Obata, Bull. Chem. Soc. Jpn., 50, 2187 (1977).

3) For [2,3]sigmatropic rearrangements of dithiocarbenes, see J. E. Baldwin and J. A. Waker, J. Chem. Soc., Chem. Commun., 1972, 354; D. A. Evans, C. L. Sims, and G. C. Andrews, J. Am. Chem. Soc., 99, 5453 (1977); T. Nakai and K. Mikami, Chem. Lett., 1978, 1243.

4) G. J. Karabatsos and R. A. Taller, Tetrahedron, 24, 3923 (1968) and references cited therein. For the stereochemical assignment via ^{13}C nmr spectroscopy, see C. A. Bunnell and P. L. Fuchs, J. Org. Chem., 42, 2614 (1977).

5) T. Nakai and K. Mikami, the accompanying paper.

6) On the basis of the geometrical assignments described above, the spectral trend means that benzene shifts the resonances of anti-S-methyl(or methylene) protons to higher fields than does those of syn-S-methyl(or methylene)protons.

7) For a pertinent discussion of the effect of aromatic solvents on the chemical shifts for aldehyde and ketone hydrazone derivatives, see ref. 4.

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