Tetrahedron Letters, Vol.28, No.4, pp 445-448, 1987 Printed in Great Britain 0040-4039/87 \$3.00 + .00 Pergamon Journals Ltd.

CORRELATION OF THE TWO TORSIONAL DEGREES OF FREEDOM ABOUT THE BONDS CONNECTING THE BRIDGEHEAD CARBONS TO THE SULFUR ATOM IN BIS(9-TRIPTYCYL) SULFIDE¹

Yuzo Kawada,* Joji Ishikawa, Hiroshi Yamazaki, Gen Koga, Shigeru Murata,[≠] and Hiizu Iwamura[≠]* Department of Chemistry, Faculty of Science, Ibaraki University, Bunkyo, Mito 310, Japan [≠]Division of Applied Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Summary: Bis(9-triptycyl) sulfides were prepared by pyrolytic extrusion of sulfur dioxide from the corresponding thiosulfonates. A pair of torsional motions about the C-S bonds in these sulfides are in strict gearing and require a barrier of 29.3 \pm 0.3 kcal/mol for gear slippage.

In the previous papers of this series² were described unique stereochemical consequences of correlation of the two torsional degrees of freedom about the bonds from the bridgehead carbons to the central atom X of bis(9-triptycyl)X molecules. In the case of the central atoms belonging to the first row of the periodic table, the two torsional motions couple so strictly into disrotation as never to miss gearing under ambient conditions. Therefore optically inactive (meso) and racemic (dl) isomers (phase isomers) are generated by identically labeling one of the three benzene rings of each 9-triptycyl moiety. It is only at very high temperatures that the strict coupling begins to disappear and the meso and dl isomers interconvert to each other. The barrier for the latter process (literally molecular gear slippage) shows a marked dependence on the central atoms: 32.3, 39.1, 42.0 kcal/mol for the methane,^{2e} the amine, 2k and the ether, 2e respectively, in the 2-chloro substituted series. However, the barrier heights remain to be determined in the case of central atoms of the second or lower row. A preliminary value (below 20 kcal/mol)^{2e} obtained for bis(2-chloro-9-triptycyl)silane suggested that there could be



meso



ULU

d (or 1)

.

a considerable decrease in the barrier on going down the periodic table and thus the meso and dl isomers might interconvert under ambient conditions. In the present paper we report successful preparations of bis(9-triptycyl) sulfides 1 and their rather unexpected strict coupling of the torsional motions about the two C-S bonds.

A synthetic route is outlined in Scheme 1. Most of the known methods for the preparation of aliphatic sulfides³ are not applicable since the alpha carbons of these sulfides are bridgehead carbons. Extrusion of sulfur dioxide from S-benzyl α -toluenethiosulfonate (RSSO₂R, R = CH₂Ph) is known to be effected either through heating in solution,⁴ by irradiation,⁵ or by pyrolysis in the absence of solvent at high temperature.⁶ Although the first method gives the highest yield of dibenzyl sulfide (72 %), an ionic mechanism through an incipient ion pair (R⁺⁻O₂SSR) is suggested and it is not applicable to the preparation of 1. The other two give only a moderate amount of the sulfide (15 ~ 22 %) through radical pathways. Since 9-triptycyl radicals have a high propensity for hydrogen abstraction⁷ and the triptycene skeletons undergo ready photorearrangement,⁸ only the third pyrolytic method is worthy of serious consideration.

Scheme 1 TpBr $\xrightarrow{1}$ BuLi TpSH \xrightarrow{DMSO} TpSSTp \xrightarrow{mCPBA} TpSSO₂Tp $\xrightarrow{\Delta}$ TpSTp (+ 2 + TpH) 3 a: Tp = 9-triptycy1 b: Tp = 2-chloro-9-triptycy1

Pyrolysis of thiosulfonates 3 in solid state under a blanket of nitrogen $(250 \sim 300 \text{ °C})$ gave moderate yield $(15 \sim 20 \text{ \%})$ of sulfides 1 along with the corresponding disulfides 2 and triptycenes $(45 \sim 50 \text{ \%})$. Sulfide 1a (needles: mp > 400 °C (from CH₂Cl₂/hexane)) was separated from 2a very efficiently through gel permeation chromatography (GPC),⁹ whereas only a partial separation was achieved for a mixture of 1b and 2b. A GPC fraction containing 1b and 2b was further separated by preparative HPLC and the second and third components (eluted order) were found to be the meso (microcrystalline plates: mp 328 ~ 329 °C) and d1 (microcrystalline plates: mp 359 ~ 360 °C) isomers of 1b, respectively.

The physical separation of the phase isomers at room temperature indicated that the barrier for the gear slippage of the sulfide must be not lower than 24 kcal/mol. The accurate kinetic and equilibrium parameters ($E_a = 29.3 \pm 0.3$ kcal/mol, log A = 12.2 ± 0.2 , K = 1.73 ± 0.01 , and $\epsilon_{dl}/\epsilon_{meso} = 1.10$ in o-dichlorobenzene) were obtained at 61 ~ 132 °C by means of classical kinetics starting from the pure meso isomer as in the previous studies.² We note a

similar magnitude of increase in the barriers (about 10 kcal/mol) on going from the methane to the ether and from the silane to the sulfide. The barriers for the gear slippage are considered to be governed by an interplay of C-X bond lengths, C-X-C bond angles, C-X stretching and C-X-C bending force constants. According to the reported values for a series of $Me_{2}X$ type molecules,⁹ the C-O and C-S bonds are both shorter than the C-C and C-Si bonds by 0.116 Å (7.6 \$) and 0.065 Å (3.5 %), respectively. The C-O stretching force constant is larger than the C-C by 0.896 mdyn/Å, but the C-S stretching constant is smaller than the C-Si by 0.300 mdyn/Å. The two structural factors are not additive in the second row and suggest a much smaller difference in the barrier heights between the silane and the sulfide. The observed similar increments in the barrier heights between the first and second row elements seem to point to the relative importance of the other two factors, i.e., a smaller C-S-C bond angle by 2.1° and a larger C-S-C bending force constant by 0.111 mdyn/Å than those of the C-Si-C. Small C-S-C angles of sulfides (98.9° in Me₂S) are well konwn. However, they are usually not small enough to generate additional stereoisomers due to restriction of the torsional degrees of freedom around the C-S bonds. In this sense, sulfides 1 are unique molecules, although the real C-S-C angle is expected to be much larger than that of dimethyl sulfide.^{2h}

In sharp contrast with tricoordinated oxygen and sulfur compounds whose barriers for configurational inversion are relatively well documented, configurational inversion of divalent oxygen and sulfur cannot be easily studied experimentally especially in acyclic compounds. Considerably high barriers have been predicted theoretically.¹¹ It is to be noted that the barrier reported in this paper provides a lower limit of configurational inversion of the divalent sulfur atom through an sp-hybridized linear transition state.

References and Notes

- (1) Part 12 of the series. See ref. 2k for part 11.
- (2) (a) Kawada, Y.; Iwamura, H. J. Org. Chem. 1980, 45, 2457. (b) Kawada, Y.; Iwamura, H. J. Am. Chem. Soc. 1981, 103, 958. (c) Kawada, Y.; Iwamura, H. <u>Tetrahedron Lett</u>. 1981, 22, 1533. (d) Kawada, Y.; Iwamura, H.; Okamoto, Y.; Yuki, H. <u>Ibid</u>. 1983, 791. (e) Kawada, Y.; Iwamura, H. J. Am. Chem. Soc. 1983, 105, 1449. (f) Koga, N.; Kawada, Y.; Iwamura, H. <u>Ibid</u>. 1983, 105, 5498. (g) Kawada, Y.; Okamoto, Y.; Iwamura, H. <u>Ibid</u>. 1983, 24, 5359. (h) Iwamura, H.; Ito, T.; Ito, H.; Toriumi, K.; Kawada, Y.; Osawa, E.; Fujiyoshi, T.; Jaime, C. J. Am. Chem. Soc. 1984, 106, 4712. (i) Koga, N.; Iwamura, H. <u>Ibid</u>. 1985, 107, 1426. (j) Koga, N.; Kawada, Y.; Iwamura, H. <u>Tetrahedron</u> 1986, 42, 1679. (k) Kawada, Y.; Yamazaki, H.; Koga, G.; Murata, S.; Iwamura, H. J. Org. Chem. 1986, 51, 1472. See also a series of papers by Mislow et al.; Bürgi, H.-B.; Hounshell, W. D.; Nachbar Jr., R. B.; Mislow, K. J. Am. Chem. Soc. 1983, 105, 1472, and the earlier works cited therein.

- (3) Sandler, S. R.; Karo, W. "Organic Functional Group Preparation", 2nd Ed., Chapt. 18, Academic Press, 1983.
- (4) Kice, J. L.; Parham, F. M.; Simons, R. M. J. Am. Chem. Soc. 1960, 82, 834.
- (5) White, R. C.; Dellinger, D. J. Chem. Research(S) 1985, 64.
- (6) Boechman, K.; Foegtle, F. Chem. Ber. 1981, 114, 1048.
- (7) Bartlett, P. D.; Green, F. D. J. Am. Chem. Soc. 1954, 76, 1088.
- (8) Kawada, Y.; Tukada, H.; Iwamura, H. <u>Tetrahedron Lett</u>. <u>1980</u>, <u>21</u>, 181. and references cited therein.
- (9) Gel permeation chromatography was performed on two JAIGEL 1H columns connected in series with a flow of 3 mL/min of chloroform on an LC-08 apparatus of Japan Analytical Industry Co. Ltd.
- (10) (a) Hayashi, M. J. Chem. Soc. Japan 1957, 78, 627. (b) Takahashi, H. <u>Ibid.</u> 1961, 82, 1304. (c) Shiro, Y.; Ohsaku, M.; Hayashi, M.; Murata, H. <u>Bull. Chem. Soc. Japan</u> 1970, 43, 609. (d) Idem. <u>Ibid.</u> 1970, 43, 619. (d) Ohno, K.; Hayashi, M.; Murata, H. J. Sci. Hiroshima Univ., <u>Ser. A;</u> Phys. Chem. 1972, 36, 121.
- (11) Cremer, D.; Kraka, E.; Gauss, J.; Bock, C. W. J. Am. Chem. Soc. 1986, 108, 4768, and references cited therein.

(Received in Japan 14 October 1986)