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BASE INDUCED SKELETAL REARRANGEMENTS VIA SPIROCYCLIC IPSO INTERMEDIATES IN DIBENZODITHIOCINIUM SALTS

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Abstract: Treatment of 6-methyl-12-oxo-5H,7H-dibenzo[b,g][1,5]-dithiocinium salt (1a) with methanolic KOH afforded the ring contracted product (2a), i. e., thiepin derivatives, trans-2a (44%) and cis-2a (19%). However, the corresponding deoxo-dithiocinium salt (1b) gave an unexpected isomer (2b) with the same thiepin skeleton. These are explained by tandem sigmatropy.

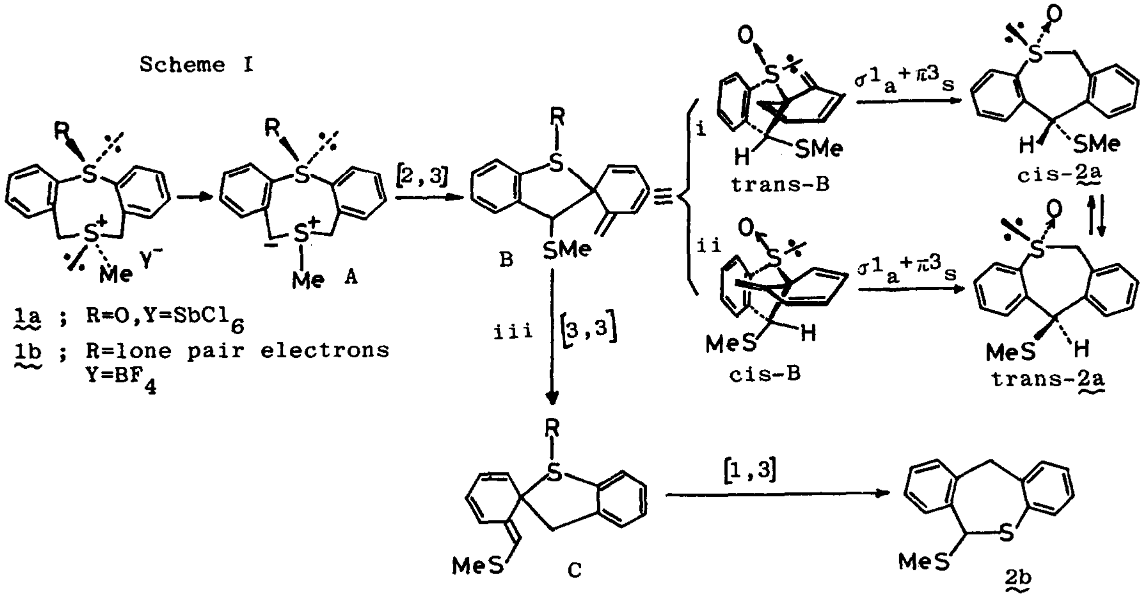
In the course of investigation on the formation of hypervalent bond (10-S-4) based on transannular interaction between the sulfur and the nitrogen in dibenzothiazocine and related compounds,[1] we encountered unexpected skeletal contraction of those to thiepin derivatives. Here we describe such novel base-induced skeletal rearrangements of dibenzodithiocinium system to give dibenzothiepin derivatives (2), which presumably proceed through tandem [2,3] and [1,3] sigmatropic shifts via spirocyclic intermediates.

When 6-methyl-12-oxo-5H,7H-dibenzo[b,g][1,5]dithiocinium hexachloroantimonate (1a)[2] was treated with methanolic KOH at room temperature for 12 h under nitrogen, a mixture of dibenzothiepin S-oxide derivatives (2a) was obtained, which was separated by TLC (SiO_2: hexane-ethyl acetate; 6:4) to give trans-2a (44%) and cis-2a (19%) as shown in Scheme I.[3]

Each pure sample of 2a reached to the equilibrium between the major and the minor isomers under the reaction conditions with the ratio of 1.55 ± 0.02, thus the major isomer was assigned to be trans-2a [1.94 (SMe), 5.12 (s, 1H) in $CDCl_3$] and the minor as cis-2a [1.96 (S-Me), 5.09 (s, 1H)] according to steric consideration. Dibenzothiepin structure of 2a was confirmed by the following transformations: (i) a mixture of trans-2a and cis-2a gave dibenzothiepin (7) in 41% yield by treatment with $HSiCl_3/LiAlH_4$. (ii) deoxygenation of trans-2a with triphenylphosphine in CCl_4/CH_3CN in the presence of CF_3CO_2H gave 6 (38%), 4 (19%), and recovered trans-2a (20%). Similarly, cis-2a afforded 6 (32%), 4 (40%), and recovered cis-2a (22%).

The structure of 4, 6, 7, and 2b were verified carefully by independent syntheses as shown in Scheme II. Reduction of 3 with $LiAlH_4$ gave the alcohol (4) and 4 afforded 5 by chlorination with $SOCl_2$. Treatment of the

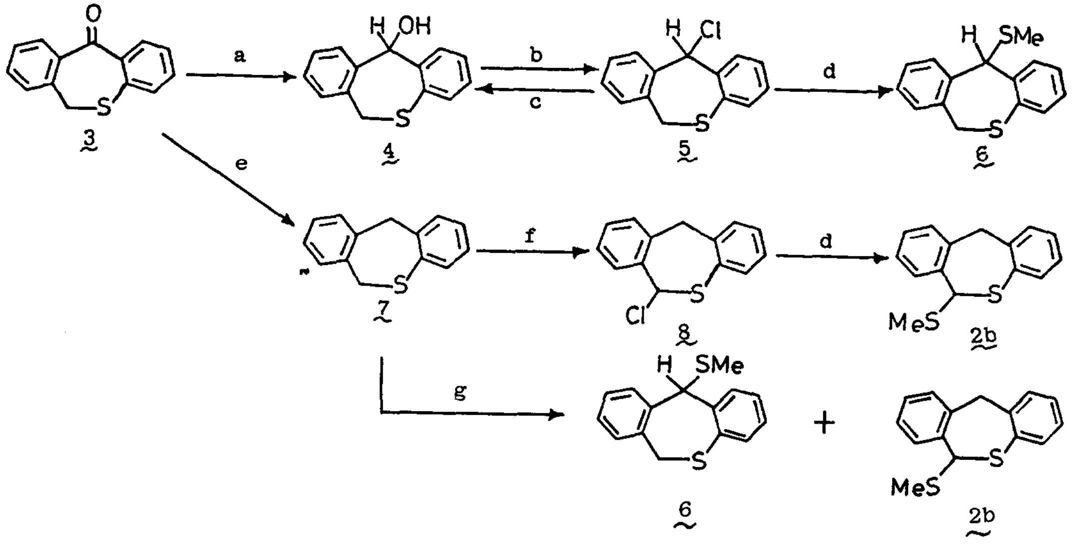
Scheme I



1a ; $R=O, Y=SbCl_6$

1b ; R=lone pair electrons $Y=BF_4$

Scheme II



a)$LiAlH_4$; b)$SOCl_2$; c)aq.NaOH ; d)MeSSMe + $LiAiH_4$
e)$LiAlH_4$; $AlCl_3$; f)SO_2Cl_2 ; BuLi + MeSSMe

chloride (**5**) with lithium methanethiolate afforded the thioether (**6**). Reduction of **3** under stronger conditions gave **7**. Chlorination of **7** with SO_2Cl_2 gave **8** via Pummerer type rearrangement and **8** was converted to **2b** with lithium methanethiolate. When **7** was deprotonated with butyllithium and reacted with dimethyl disulfide, **6** and **2b** were obtained almost in equal amount. It was further exemplified that there was not any equilibration between **6** and **2b** under reaction conditions.

Thus, the present rearrangement of **1a** is explained by Sommelet-Hauser type rearrangement of the ylide (A) to form the ipso intermediates (cis-B and trans-B), which suffer further 1,3-sigmatropy to afford the corresponding trans-**2a** and cis-**2a**, facilitated by C-S bond fission according to their strained structure.[4] It could not be determined which path (i via trans-B or ii via cis-B) was more favored, because there was equilibration between cis-**2a** and trans-**2a**.

On the other hand, the sulfide (**1b**) gave **2b** in 29% yield, without **6** (the product expected by direct [1,3] sigmatropy from B) under the same conditions.[5] Since no rearrangement of **6** into **2b** was observed under the reaction conditions, the formation of **2b** is understood by [3,3] sigmatropy of B to produce C, which suffers the [1,3]shift via C-S bond fission to afford **2b**. It is not yet clear why B affords the product (**2a**) directly for the sulfoxide (**1a**) and , on the other hand, B suffers an extra sigmatropy to C prior to give the product (**2b**) for the sulfide (**1b**).[6]

Related rearrangement of thiophenanthrene ylide via spirocyclic intermediate was recently reported by M. Hori et al.[7] but 1,5-sigmatropy of the intermediate proceeded only under very severe conditions (200 °C, 4h) as compared with the present result.

Although, there can be different rationalization to understand the present unexpected rearrangement of **1a** and **1b**,[8] it is attractive to invoke the ipso intermediates (B and C) and this will stimulate the stereochemical consideration on these kinds of sigmatropy.

References and Notes

1) K. Akiba, K. Takee, K. Ohkata, and F. Iwasaki, J. Am. Chem. Soc. **105**, 6965 (1983); K. Ohkata, K. Takee, and K. Akiba, Tetrahedron Lett. **24**, 4859 (1983); K Ohkata, K. Takee, and K. Akiba, Bull. Chem. Soc. Jpn. **58**, 1946 (1985).

2) **1a**: *mp 178-181.5 °C; the conformation has been shown to be boat-chair* and the oxygen and the methyl are trans by X-ray analysis: K. Ohkata, K. Okada, and K. Akiba, Tetrahedron Lett. **26**, 4491 (1985).

1b: mp 212.5-214.0 °C; ^1H NMR (δ, CD_3CN) 3.19 (s, 3H), 4.56, 5.72 (ABq, J = 13 Hz, 4H), 7.33-7.65 (m, 6H), and 7.85-8.06 (m, 2H).

3) trans-**2a**: Mass (m/e) 274 (M^+); IR (neat) 1020 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 1.94 (s, 3H), 4.25, 4.94 (ABq, J = 14.5 Hz, 2H), 5.12 (s, 1H), 7.1-7.6 (m,

7H), 7.9-8.0 (m, 1H).

cis-2a: Mass (m/e) 274 (M^+); IR (neat) 1020 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 1.96 (s, 3H), 4.37, 5.82 (ABq, J = 13 Hz, 2H), 5.09 (s, 1H) 7.2-7.6 (m, 7H), 7.8-8.0 (m, 1H).

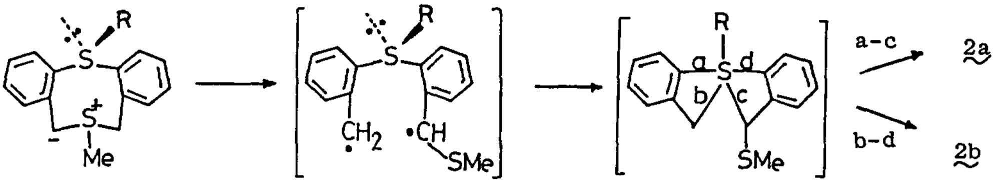
4) In Scheme I, the products due to 1,3-sigmatropy of formal $[{}_{\sigma}1_{a} + {}_{\pi}3_{s}]$ fashion is shown, if 1,3-sigmatropy of formal $[{}_{\sigma}1_{s} + {}_{\pi}3_{a}]$ fashion takes place, cis-B affords cis-2a and trans-B does trans-2a. There can be no evidence at present to discriminate the two possibility, we prefer the one shown in Scheme I.

5) 2b: mp 86-87 °C; Mass (m/e) 258 (M^+); ^1H NMR (δ, $CDCl_3$) 2.06 (s, 3H), 4.10, 4.60 (ABq, J = 13.9 Hz, 2H), 5.42 (s, 1H), and 7.0-7.3 (m, 8H).

6) Compounds described here (1a, 1b, trans-2a, and 2b) gave correct elemental analyses.

7) M. Hori, T. Kataoka, H. Shimizu, and O. Komatsu, J. Chem. Soc. Chem. Commun. 883 (1985).

8) If 1a and 1b rearrange by Stevens type reaction involving diradical D and subsequent trapping of the diradical in D by the sulfur atom produces sulfurane E, selective reductive coupling by a-c fission gives 2a and that by b-d fission gives 2b.



D E

Intramolecular trapping of a radical by the sulfide group is known to be quite effective, but the implication of this mechanism to the present system has no evidence at present. C. W. Perkins, J. C. Martin, A. J. Arduengo, W. Lau, A. Alegria, and J. K. Kochi, J. Am. Chem. Soc. 102, 7753 (1980).

9) The authors are indepted partially to Grant-in Aid for Scientific Research (No. 60303004) administered by the Ministry of Education, Science, and Culture of Japanese Government.

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