Tetrahedron Letters, Vol.32, No.34, pp 4359-4362, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

REACTIONS OF AZATHIABENZENE ANION WITH ELECTROPHILES. FORMATION AND X-RAY ANALYSIS OF NOVEL HETEROCYCLIC COMPOUNDS FROM THE REACTION WITH CARBOXYLIC ESTER

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Abstract: The anion (**2**) generated from 9-methyl-10-aza-9-thiaphenanthrene (**1**) reacted with carboxylic ester to give the spiro compounds (**9a**), (**9b**) via Sommelet-Hauser rearrangement, whose structures have been confirmed by an X-ray crystal structure determination of (**9a**).

Recently, we have reported novel 1,2-shift of benzyl group of cyclic sulfilimines, 9-benzyl-10-aza-9-thiaphenanthrenes, affording 6-benzyl-6H-dibenzo [c,e] [1,2] thiazines, which is rarely observed in sulfilimine chemistry.[1] In continuous studies on the chemistry of azathiabenzene derivatives, we investigated the reactivities of azathiabenzene anion generated from alkyl-substituted azathiaphenanthrene and found the formation of novel spiro compounds from the reaction with carboxylic ester.

First, we examined the generation of azathiaphenanthrene anion (**2**) by the deprotonation of 9-methyl-10-aza-9-thiaphenanthrene (**1**) with LDA in THF, since the methyl hydrogen of (**1**) is considered to be acidic due to the positive sulfur atom.[2] The red colored solution was obtained and then quenched with methyl or ethyl iodide to afford 9-ethyl (**3a**) or 9-propyl-10-aza-9-thiaphenanthrene (**3b**) in the yields of 31% or 44%, respectively (Scheme 1). This result indicated the distinct generation of azathiaphenanthrene anion (**2**). Therefore, we next quenched the red solution with trimethylsilyl chloride, and obtained no desired trimethylsililated azathiaphenanthrene (**4**), but ring-expanded product (**5**)[3] in 27% yield, which was presumably formed via sulfonium ylide intermediate derived from the expected compound (**4**) by 1,3-proton shift as shown in Scheme 1.

With the intention of preparing 9-acylmethyl-10-aza-9-thiaphenanthrenes, we next carried out the reaction of the anion (**2**) with ethyl acetate (Scheme 2). However, we could not get the expected 9-acetylmethyl-10-aza-9-thiaphenanthrene (**6a**), but a novel spiro compound (**9a**), mp 203-205 °C, as white prisms in 48% yield. Microanalytical and mass spectral data (M^+, m/z 255) indicated a molecular formula $C_{15}H_{13}NOS$ for this compound. It showed an IR hydroxyl absorption at 3130 cm^{-1} and ^{1}H-NMR peaks at δ 1.07 and 3.85 due to methyl group and methine proton, as a singlet signal, respectively. The

Selected bond distances and angles are provided in Figure 1.[7] In the crystal structure of (**9a**), methyl group occupies cis configuration to benzothiophene ring.

A possible mechanism for the formation of the spiro compounds (**9**) is shown in Scheme 2. A nucleophilic attack of the carbanion of the azathiaphenanthrene anion (**2**) on the carbonyl group of the ester gives 9-acylmethylazathiaphenanthrenes (**6**) after the loss of ethoxide ion. Possibly because of instability of azathiaphenanthrene structure (**6**), it is readily converted to the sulfonium ylide intermediate (**7**), via 1,3-proton shift, whose carbanion attacks on the aromatic carbon (C-4a) along with the cleavage of the S-N bond to afford intermediate (**8**) (Sommelet-Hauser type rearrangement). Finally, the nitrogen atom of the intermediate (**8**) attacks on the proximate carbonyl group to give the final product (**9**).

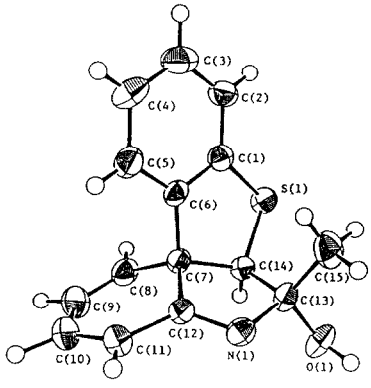


Figure 1. Molecular structure of (**9a**). Selected bond distances (Å) and angles (°) are: S(1)-C(1)=1.763(4), S(1)-C(14)=1.810(4), C(1)-C(6)=1.399(5), C(6)-C(7)=1.532(5), C(7)-C(14)=1.538(5), C(7)-C(12)=1.527(5), N(1)-C(12)=1.281(4), N(1)-C(13)=1.481(5), C(13)-C(14)=1.565(5), C(7)-C(8)=1.518(5), C(8)-C(9)=1.325(6), C(9)-C(10)=1.459(6), C(10)-C(11)=1.342(6), C(11)-C(12)=1.444(5); C(1)-S(1)-C(14)=91.0(2), S(1)-C(14)-C(7)=108.5(2), C(6)-C(7)-C(14)=105.2(3), C(7)-C(14)-C(13)=104.1(3), N(1)-C(13)-C(14)=104.0(3), C(12)-N(1)-C(13)=109.9(3), C(12)-C(7)-C(14)=99.9(3), C(7)-C(12)-N(1)=115.7(3), C(6)-C(7)-C(12)=114.6(3), S(1)-C(14)-C(13)=117.0(3), C(6)-C(7)-C(8)=107.8(3), C(14)-C(13)-C(15)=116.5(3), C(8)-C(7)-C(12)=110.9(3), C(7)-C(12)-C(11)=119.1(3).

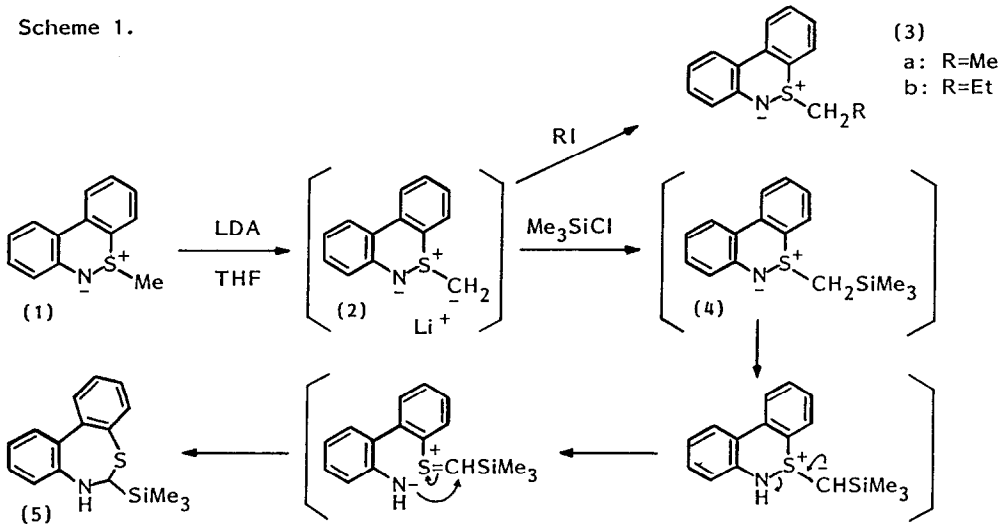
Table 1. Crystallographic Data for (**9a**)

(a) Crystal parameters
formula: $C_{15}H_{13}NOS$ size(mm): 0.20x0.15x0.2 color: colorless
crystal system: triclinic space group: P1(#2) T: 23 °C
a= 8.599(3)Å α= 97.75(3)° V= 629.6(4)Å^3
b=10.180(4)Å β=116.37(2)° Z= 2
c= 8.234(2)Å γ= 77.42(3)° μ(Mo-K α)cm^{-1}: 2.32

(b) Data collection
diffractometer: Rigaku AFC5R radiation: Mo-K α wave length: λ= 0.71069Å
scan range: $5° \leqq 2\theta \leqq 55°$ standard reflection: 3 standards/150 reflection
independent reflection: 2790 Rint: 0.030

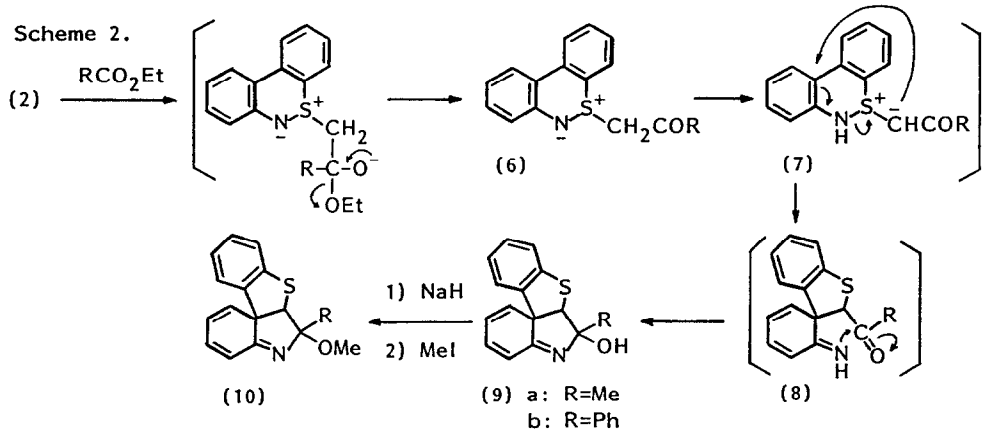
(c) Refinement
R: 0.045 Rw: 0.048 GOF: 1.21

Scheme 1.



^{13}C-NMR spectrum showed two quarternary carbon signals at δ 69.5 and 100.8, which are assignable to the spiro carbon and tertiary alcoholic carbon atoms, respectively, and sp^3 tertiary carbon signal assigned to C-6 at δ 66.3. Similarly, the reaction of the anion (**2**) with ethyl benzoate gave the corresponding spiro product (**9b**),[3] mp 187-189 °C as pale yellow prisms in 39% yield. The hydroxyl groups of the above spiro compounds (**9a**) and (**9b**) were easily methylated by adding methyl iodide after treatment with sodium hydride in THF to give the corresponding methoxy compounds (**10a**)[3] and (**10b**)[3] in 48% and 94% yields, respectively. The structure of the compound (**9a**) was confirmed by an X-ray analysis (Figure 1). Crystallographic data are summarized in Table 1. Data were collected using ω-2 θ scans. TEXSAN crystallographic software package[4] was utilized for all calculations. The structure was solved by a direct methods[5] and difference Fourier techniques, and refined by full-matrix least-square analysis.[6] The non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were treated isotropically.

Scheme 2.



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2. Y. Tamura, H. Matsushima, M. Ikeda, and K. Sumoto, Synthesis, **1976**, 35.
3. (**5**): yellow oil, IR (NaCl): 3380 cm^{-1} (NH); ^{1}H-NMR ($CDCl_3$) δ : 0.17 (9H, s, 3xMe), 3.6-3.80 (1H, br, NH), 4.24 (1H, s, CH), 7.02-7.54 (8H, m, ArH); MS m/z: 285 (M^+), 184 (base); ^{13}C-NMR ($CDCl_3$) δ : -3.09 (q), 68.63 (d), 122.90 (d), 123.37 (d), 127.36 (d), 128.49 (d), 128.96 (d), 131.05 (d), 132.36 (d), 133.88 (d), 134.74 (s), 136.78 (s), 144.30 (s), 146.09 (s); High-resolution MS m/z: 285.0990 (Calcd for $C_{16}H_{19}NSSi$, 285.1006). (**9b**): IR (KBr): 3060 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ : 1.73 (1H, br, OH), 3.93 (1H, s, CH), 6.01-6.08 (1H, m, olefinic H), 6.26-6.33 (1H, m, olefinic H), 6.53-7.49 (11H, m, olefinic and ArH); ^{13}C-NMR ($CDCl_3$) δ : 65.8 (d), 71.1 (s), 104.6 (s), 120.5 (d), 122.3 (d), 123.4 (d), 124.1 (d), 125.0 (d), 126.3 (d), 127.8 (d), 128.4 (d), 129.2 (d), 136.4 (d), 136.5 (d), 136.9 (s), 140.0 (s), 145.2 (s), 177.7 (s); MS m/z: 317 (M^+), 105 (base); Anal. Calcd for $C_{20}H_{15}NOS$: C, 75.68; H, 4.76; N, 4.41. Found: C, 75.75; H, 4.79; N, 4.44. (**10a**): yellow prisms, mp 79-80 °C; ^{1}H-NMR ($CDCl_3$) δ : 1.28 (3H, s, Me), 3.14 (3H, s, OMe), 3.97 (1H, s, CH), 6.03-6.08 (1H, m, olefinic H), 6.29-6.33 (1H, m, olefinic H), 6.68-6.70 (2H, m, olefinic H), 6.94-7.28 (4H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ : 20.6 (q), 50.4 (q), 63.8 (d), 70.3 (s), 105.0 (s), 120.2 (d), 122.1 (d), 123.3 (d), 123.8 (d), 125.4 (d), 129.1 (d), 135.6 (d), 135.9 (d), 136.1 (s), 140.3 (s), 172.6 (s); MS m/z: 269 (M^+), 197 (base); Anal. Calcd for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20. Found: C, 71.08; H, 5.72; N, 5.15. (**10b**): pale yellow prisms, mp 128-130 °C; ^{1}H-NMR ($CDCl_3$) δ : 3.42 (3H, s, OMe), 4.07 (1H, s, CH), 5.99-6.11 (1H, m, olefinic H), 6.28-6.31 (1H, m, olefinic H), 6.51-6.54 (1H, m, olefinic H), 6.75-7.56 (10H, m, olefinic and ArH); ^{13}C-NMR ($CDCl_3$) δ : 52.3 (q), 67.4 (d), 70.1 (s), 108.9 (s), 120.2 (d), 122.0 (d), 122.5 (d), 123.8 (d), 124.9 (d), 125.7 (s), 126.2 (d), 127.5 (d), 128.0 (d), 128.5 (s), 128.6 (d), 136.1 (d), 136.4 (d), 139.5 (s), 175.6 (s); MS m/z: 331 (M^+), 229 (base); Anal. Calcd for $C_{21}H_{17}NOS$: C, 76.10; H, 5.17; N, 4.23. Found: C, 75.91; H, 5.24; N, 4.17.
4. TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).
5. C. J. Gilmore; MITHRIL- an integrated direct methods computer program. J. Appl. Cryst. 17, 42-46, Univ. of Glasgow, Scotland (1984). P. T. Beurskens; DIRDIF- Direct Methods for Difference Structures- an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed. Nijmegen, Netherlands.
6. Function minimized: $\Sigma w(|Fo| - |Fc|)^2$
7. Full details of the crystal structure analysis including the tables of atomic coordinates and thermal parameters have been deposited in the Cambridge Crystallographic Data Centre.

(Received in Japan 22 March 1991)