Tetrahedron Letters, Vol.31, No.48, pp 7021-7022, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

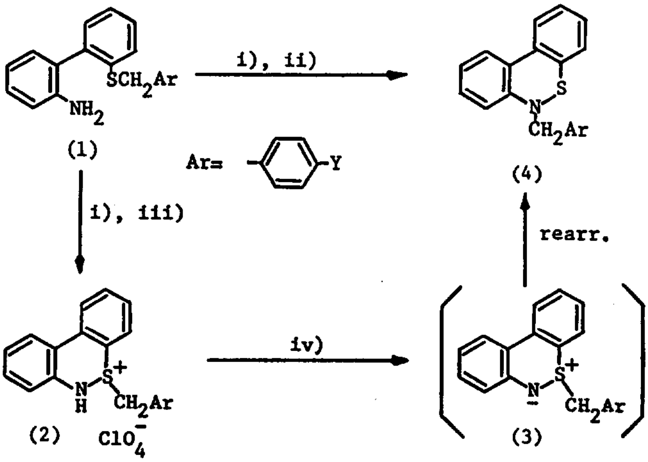
THERMAL REARRANGEMENT OF 9-BENZYL-10-AZA-9-THIAPHENANTHRENES

Hiroshi Shimizu, Koji Ikedo, Koji Hamada, Harutoshi Matsumoto, Michinori Ozawa,
Tadashi Kataoka, and Mikio Hori*
Gifu Pharmaceutical University, 6-1, Mitahora-higashi 5-chome, Gifu 502, Japan

Abstract: 9-Benzyl-10-aza-9-thiaphenanthrenes (**3**) generated from 9-benzyl-10-aza-9-thiaphenanthrenium salts (**2**) by treatment with base underwent thermal 1,2-benzyl migration to give the corresponding 6-benzyl-6H-dibenzo[c,e][1,2]thiazines (**4**).

In our earier reports, we described the thermal decomposition of benzo-fused azathiabenzenes, 9-alkyl-10-aza-9-thiaphenanthrenes; 9-methyl derivative underwent thermal ring expansion reaction to give dibenzothiazepine derivative, whereas 9-ethyl derivative underwent dealkylation to furnish dibenzothiazine derivative.[1] In the course of further studies on the thermal stability of other several 9-substituted 10-aza-9-thiaphenanthrenes, we found novel 1,2-rearrangement of 9-benzyl derivatives.

With the intention of preparing 9-benzyl-10-aza-9-thiaphenanthrene (**3a**), we carried the cyclization of 2-amino-2'-benzylthiobiphenyl(**1a**) with N-chlorosuccinimide (NCS) in dichloromethane at -50°C, and successively deprotonated azasulfonium salt formed in solution with an aqueous KOH solution at 0°C. However, we could not get the expected 9-benzyl-10-aza-9-thiaphenanthrene (**3a**), but 6-benzyl-6H-dibenzo[c,e][1,2]thiazine (**4a**) in moderate yield. This suggested that 9-benzyl derivative (**3a**) initially formed was unstable to be isolated and readily underwent thermal 1,2-rearrangement of S-benzyl



Reagents: i) NCS or t-BuOCl-CH_2Cl_2; ii) aq NaOH soln.; iii) $AgClO_4$;
iv) aq NaOH soln-CH_2Cl_2 or n-BuLi-THF.

group. In order to verify this, we performed the deprotonation of isolated 9-benzyl-10-aza-9-thiaphenanthrenium perchlorate (**2a**) which was easily prepared in 63 % yield by adding silver perchlorate to the reaction mixture of (**1a**) and NCS, to afford (**4a**) in 50% yield. This type of 1,2-shift of the alkyl substituent on sulfur atom to nitrogen atom of sulfilimine is quite rare, although the 1,2-imino shift from the sulfur atom to α-methylene carbon atom has been well known.[2,3] To our knowledge, there is a single recent report on the thermal (at 60 °C) 1,2-alkyl shift of highly strained (four-membered ring) exo-cyclic sulfilimines, in which the high ring strain is considered to cause the C-S bond fission, making the 1,2-alkyl shift possible.[4] Oae et al. have estimated the 1,2-alkyl shifted intermediate in the plausible mechanism for the formation of final products resulted from the thermal decomposition (180 °C in sealed tube) of acyclic N-tosylsulfilimines.[5,6]

Similarly, other 2-amino-2'-benzylthiobiphenyl derivatives (**1**) were treated with NCS or t-butylhypochlorite (t-BuOCl) for the cyclization, followed by deprotonation with base at 0 °C to give the corresponding 1,2-rearranged products (**4**) in moderate to good yield. n-Butyllithium was used for the deprotonation of the isolated azasulfonium perchlorates (**2a**, **2b**) in dry THF, while an aq NaOH solution was effectively used for the deprotonation of no isolated azasulfonium salts (**2c-h**) in dichloromethane. The results are summarized in Table. We are now under investigation on the detailed mechanism of this interesting 1,2-rearrangement of azathiaphenanthrenes.

Table. Synthesis and Thermal Rearrangement of 9-Benzyl-10-aza-9-thiaphenanthrenes (3)

Biphenyl (1)	Y	Chlorinating agent	Yield (%) of (2)	Base	Yield (%) of (4)
(1a)	H	NCS	63	BuLi	50[b]
(1b)	Me	NCS	69	BuLi	57[b]
(1c)	OMe	t-BuOCl	46	NaOH	21[c]
(1d)	Br	t-BuOCl	90	NaOH	56[c]
(1e)	Cl	t-BuOCl	a	NaOH	28
(1f)	F	t-BuOCl	a	NaOH	28
(1g)	$2,4\text{-}Cl_2$	t-BuOCl	a	NaOH	40
(1h)	NO_2	t-BuOCl	a	NaOH	57

a No isolation of the perchlorate (2), b Based on the perchlorate (2), c Based on the biphenyl (1)

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(Received in Japan 30 August 1990)