Pergamon

Tetrahedron Letters 40 (1999) 95–96

TETRAHEDRON
LETTERS

Novel Polar Cycloaddition of 1,2-Thiazinylium Salt

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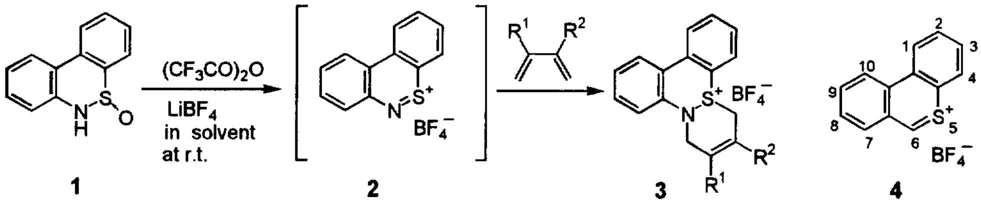
Received 13 September 1998; accepted 23 October 1998

Abstract: *Dibenzo[c,e][1,2]thiazinylium tetrafluoroborate underwent polar cycloaddition with several 1,3-butadienes to afford new sulfur-nitrogen-containing sulfonium heterocycles in good yields. The cycloaddition with unsymmetrical 1,3-butadiene, isoprene afforded two regioisomeric adducts. Deprotonation of the cycloadduct underwent ring transformation to yield a pyrrole derivative.* © 1998 Elsevier Science Ltd. All rights reserved.

In our previous papers, we reported novel [2$^+$+4]-type polar cycloaddition of 1- and 2-benzothiopyrylium salts and dibenzo[*c,e*]thiopyrylium salts with several 1,3-butadienes, affording the corresponding cycloadducts having sulfur at a bridgehead position in high yields.[1]

In our continuous studies on polar cycloaddition of thiopyrylium salts, we next planned to explore polar cycloaddition of sulfur-nitrogen bond-containing six-π heterocyclic compounds, 1,2-thiazinylium salts, which have isoelectronic structures, with thiopyrylium salts and therefore are expected to undergo the cycloaddition across the N=S bond. In this communication, we describe successful polar cycloaddition of dibenzo[*c,e*][1,2]thiazinylium salt **2** with several 1,3-butadienes, and ring transformation of the cycloadduct obtained.

Treatment of dibenzo[*c,e*][1,2]thiazinylium tetrafluoroborate (**2**), generated *in situ* from the reaction of dibenzo[*c,e*][1,2]thiazine 5-oxide (**1**)[2] with trifluoroacetic anhydride in the presence of lithium tetrafluoroborate in THF, with 2,3-dimethyl-1,3-butadiene (2 mol. equiv.) at room temperature for 19 h afforded the cycloadduct **3a**[3] in only 6% yield (Scheme 1). In order to improve the yield of the cycloadduct, we closely examined the solvent effect for the cycloadditions. The reaction in 1,2-dichloroethane resulted in high yield (89%) of the product in shorter reaction time (15 min.) as summarized in Table 1, probably because of high solubility of the salt **2** in that solvent. Several other 1,3-butadienes reacted similarly in 1,2-dichloroethane with the salt **2** to afford the corresponding cycloadducts **3**, respectively, as listed in Table 1. Cycloaddition of isoprene afforded an inseparable mixture of two regioisomeric cycloadducts **3c** and **3d** in the ratio of 3.5:1 (determined by ^{1}H-NMR spectroscopy).[4] It is noteworthy to compare this result with our previous findings[1d] that cycloaddition of isoprene with dibenzo[*c,e*]thiopyrylium salt **4** proceeded regiospecifically to give only a single isomer, whose regiostructure is similar to that of the major cycloadduct **3c** obtained from the above 1,2-thiazinylium salt **2**. These interesting results would be reasonably explained by comparison of Frontier Molecular Orbital coefficients in the above two different salts **2** and **4**. These cycloadditions would be considered to be $\mathrm{LUMO_{salt}}$-$\mathrm{HOMO_{diene}}$ interacted reactions. According to MOPAC 93 PM3 calculation,[5] the difference in magnitude between the nitrogen and sulfur LUMO coefficients of the salt **2** [N (0.552), S (-0.465)] is smaller than that between the carbon and sulfur LUMO coefficients of the salt **4** [$C_{(6)}$ (0.616), S (-0.469)]. This smaller difference in magnitude between the sulfur-nitrogen



Scheme 1

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PII: S0040-4039(98)02286-2

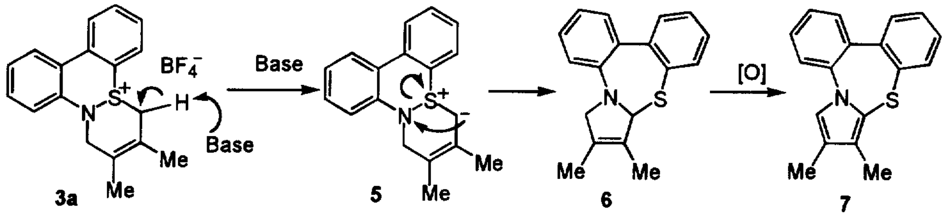
LUMO coefficients of 1,2-thiazinylium salt **2** might make the cycloaddition less regioselective, thus giving two regioisomers.

Table 1. Polar Cycloadditions of Dibenzo[*c*,*e*][1,2]thiazinylium Salt **2** with 1,3-Butadienes

Entry	1,3-Butadiene		Solvent	Time(h)	Product			
	R^1	R^2				R^1	R^2	Yield(%)
1	Me	Me	THF	19	**3a**	Me	Me	6
2	Me	Me	Ether	13	**3a**	Me	Me	38
3	Me	Me	CH_2Cl_2	12	**3a**	Me	Me	69
4	Me	Me	$ClCH_2CH_2Cl$	0.25	**3a**	Me	Me	89
5	Ph	Ph	$ClCH_2CH_2Cl$	18	**3b**	Ph	Ph	83
6	Me	H	$ClCH_2CH_2Cl$	4	**3c***	Me	H	54
					3d*	H	Me	16
7	H	H	$ClCH_2CH_2Cl$	15	**3e**	H	H	56

*These compounds were obtained as an inseparable mixture (**3c** /**3d** =3.5)

We next studied the ring transformation of the cycloadduct **3a** by treating with strong bases. Treatment of the cycloadduct **3a** with sodium methoxide in methanol at room temperature for 30 min. afforded a pyrrole derivative **7** in 58% yield.[7] Similarly, deprotonation with LDA in THF at -78 °C for 15 min. also resulted in the formation of **7** in similar yield. For the formation of the product **7** we propose the mechanism involving amino group migration to the ylide carbon of amino sulfonium ylide intermediate **5** as depicted in Scheme 2.



Scheme 2

REFERENCES AND NOTES

1. (a) H. Shimizu, S. Miyazaki, T. Kataoka, M. Hori and O. Muraoka, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 3129. (b) H. Shimizu, S. Miyazaki, T. Kataoka and M. Hori, *J. Chem. Soc., Perkin Trans. 1*, **1995**, 1583. (c) H. Shimizu, S. Miyazaki and T. Kataoka, *J. Chem. Soc., Perkin Trans. 1*, **1996**, 2227. (d) H. Shimizu, S. Miyazaki and T. Kataoka, *Tetrahedron*, **1997**, *53*, 4611.
2. Dibenzo[c,e][1,2]thiazine 5-oxide (1) was prepared by oxidative cyclization of 2-amino-2'-mercaptobiphenyl[6] with iodine in $THF\text{-}H_2O$, colorless prisms (CH_2Cl_2-hexane); mp. 185-186 °C (dec.); IR (KBr) cm^{-1}: 3130 (NH), 1040 (SO); MS *m/z*: 215 (M^+); ^1H-NMR ($CDCl_3$) δ: 7.26-7.33 (m, ArH), 7.50-7.61 (m, ArH), 7.61-7.72 (m, ArH), 7.74-7.88 (m, ArH), 7.89 (d, J=7 Hz, ArH), 8.27-8.50 (m, ArH), 10.43 (br. s, NH).
3. Satisfactory analytical data were obtained for all new compounds. **3a**: colorless prisms (CH_2Cl_2-ether); mp. 196-198 °C; IR (KBr) cm^{-1}: 1000-1020 (BF_4^-); ^1H-NMR ($CDCl_3$) δ: 1.63 (s, CH_3), 1.77 (s, CH_3), 3.74 and 3.88 (each d, J=16 Hz, SCH_2), 4.32 (s, NCH_2), 7.02-8.08 (m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 16.9 (q), 20.0 (q), 37.8 (t), 52.5 (t), 116.2 (s), 118.7 (d), 122.6 (s), 123.2 (s), 125.3 (s), 125.6 (d), 126.3 (s), 126.3 (d), 127.0 (d), 130.3 (d), 131.8 (d), 136.3 (d), 136.9 (s).
4. ^1H-NMR ($CDCl_3$) for **3c**, δ: 1.95 (s, CH_3), 4.02 (d, J=16 Hz, *SCHH*), 4.16 (dd, J=7, 16 Hz, SCH*H*), 4.42 (d, J=19 Hz, NC*H*H), 4.54 (d, J=19 Hz, NCH*H*), 5.74 (d, J=7 Hz, CH=); for **3d**, δ: 3.73 (dd, J=6, 16 Hz, NC*H*H), 3.79 (dd, J=16, 6 Hz, NCH*H*), 5.96 (br. S, CH=).
5. The calculation of the two cations **2** and **4** was performed with The PM3 hamiltonian by "WinMOPAC v1.0 (Fujitsu Ltd.) for Windows 95 (Microsoft Inc.)", which is based on the MOPAC93 of Dr. J.J.P. Stewart and Fujitsu Ltd., Tokyo Japan.
6. H. Shimizu, K. Ikedo, K. Hamada, M. Ozawa, H. Matsumoto, K. Kamata, H. Nakamura, M. Ji, T. Kataoka and M. Hori, *J. Chem. Soc., Perkin Trans. 1*, **1991**, 1733.
7. **7**: colorless prisms (CH_2Cl_2-hexane); mp. 185-186 °C; MS m/z: 277 (M^+); ^1H-NMR ($CDCl_3$) δ: 2.01 (s, CH_3), 2.10 (s, CH_3), 6.80 (s, CH of pyrrole), 7.25-7.30 (m, ArH), 7.33-7.48 (m, ArH), 7.56-7.58 (m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 9.7 (q), 10.6 (q), 120.2 (d), 121.0 (s), 121.7 (s), 123.9 (s), 124.3 (d), 125.8 (d), 128.4 (d), 128.6 (d), 129.0 (d), 131.2 (d), 131.4 (d), 131.7 (d), 135.2 (s), 137.7 (s), 139.3 (s), 142.8 (s).