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Cycloaddition Reactions of Azatrienes with Sulfene

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ABSTRACT

Unprecedented cycloaddition reactions of azatrienes (**1**) with sulfene leading to the synthesis of functionalized thiazine-dioxide derivatives (**5**) are described. The reactions were found be highly regioselective resulting in the formation of only [4 + 2] cycloadducts.

Keywords: Azadiene; Azatriene; Cycloaddition; Sulfene; Thiazine-Dioxide

1. Introduction

1-Azadienes are remarkably efficient precursors for the synthesis of nitrogen-containing heterocycles [1-10]. The presence of multiple reactive sites makes them excellent candidates for various synthetic manipulations. For example, α,β-unsaturated imine can participate as a dienophile in a Michael type 1,4-addition (Rxn 1, **Figure 1**), or in a 1,2-addition (Rxn 2, **Figure 1**). Morever, depending upon the reaction partner, 1-azadiene can react as 2π (Rxn 3, **Figure 1**) or 4π (Rxn 4, **Figure 1**) component in the cycloaddition reactions. It is believed that the electron density in the 1-azadiene system is a significant factor that defines its reactivity. The presence of electron-donating groups (-NR_2, -OR, -R, -OSi) typically on nitrogen atom increases their reactivity towards electrophiles (Rxn 5, **Figure 1**) or electron deficient dienophiles in the hetero Diels-Alder (HDA) reactions [11-13]. On the other hand, the presence of electron-withdrawing groups (-COR, -COOR, -SO_2) makes them prone to the attack of nucleophiles or electron rich dienophiles in the inverse electron-demand HDA reactions [14,15]. However, the 4π participation of the 1-azadienes is reported to suffer from low conversion, competitive [2 + 2] addition, and low diene reactivity due to an unfavorable s-*cis*/s-*trans* equilibrium [16,17]. In addition the tautomerization of substituted 1-azadienes to enamines precludes the [4 + 2] cycloaddition due to the instability of endocyclic enamine products. Consequently, only a limited number of 1-aza-buta-1,3-diene structural variations and modified or restricted reaction conditions have been introduced that have permitted the productive 4π participation of α,β-unsaturated imines in [4 + 2] cycloaddition reactions.

Literature study reveals that the cycloaddition reactions of highly reactive heterodienophile sulfene have not extensively been explored with the C=N double bond [18].

Recently, we reported a single pot synthesis of stable cross-conjugated azatrienes **1** (**Scheme 1**) along with the tandem [2 + 2] cycloaddition and highly facile [3,3]-sigmatropic rearrangements in their reactions with conjugated ketenes, leading to facile synthesis of functionalized azocinone derivatives [19]. In connection with our ongoing interest in this research area, we widened our study to the cycloaddition reactions of azatrienes with sulfene dienophile. To the best of our knowledge, this is a first report where the [4 + 2] cycloadditions of 1-azadienes are carried out with the sulfene.

2. Results and Discussion

The cycloadditions were realized by the dropwise addition of a solution of methanesulfonyl chloride (2*eq.*) to a cooled dichloromethane solution of azatrienes **1** [19,20] and triethylamine (3*eq.*). The reactions were found to be highly regioselective leading to the exclusive formation of cycloadducts **5** without any traces of corresponding [2 + 2] adducts **6** (**Scheme 1**).

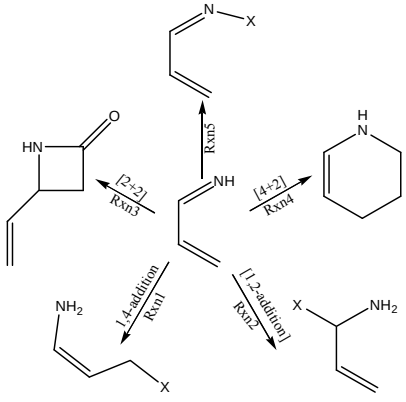

Figure 1. Different reaction types of 1-azadiene system.

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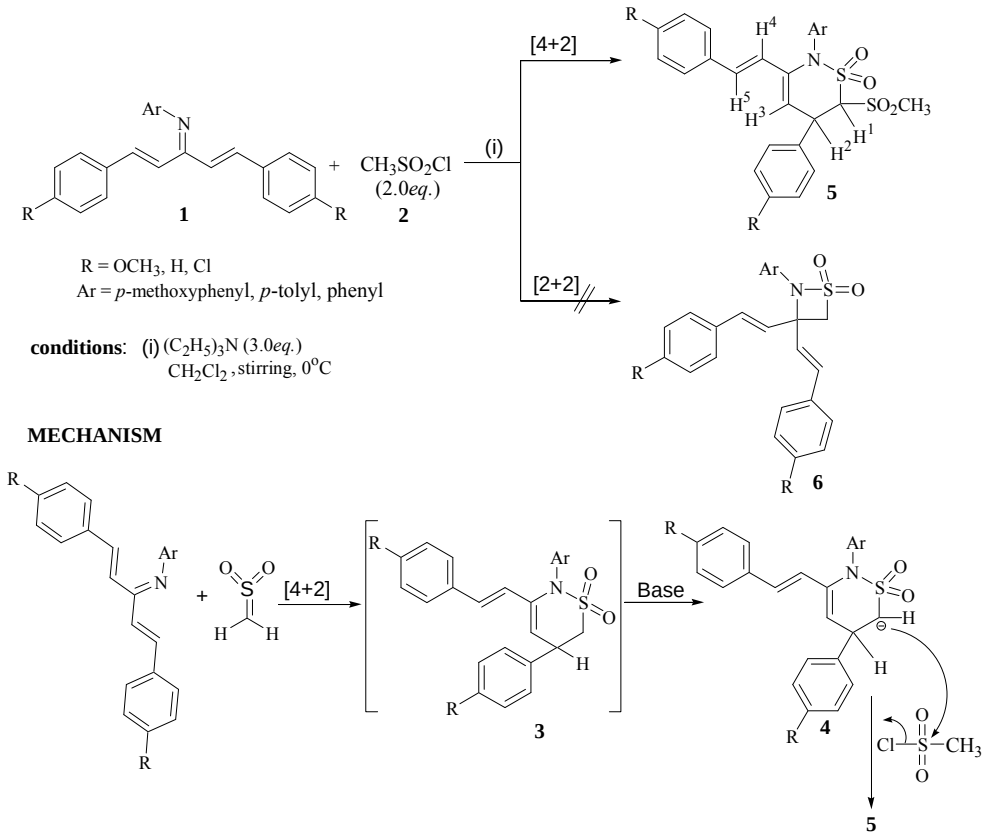

Scheme 1. Synthetic route and mechanism for the preparation of thiazine-dioxide derivatives from cycloaddition reactions of azatrienes (1) with sulfene.

The solid compounds, isolated after column chromatography, were characterized as thiazine-dioxide derivatives **5** on the basis of their available spectral data and analytical evidence. The plausible mechanistic pathway followed in these reactions involved the initial formation of [4 + 2] cycloadduct **3** as an intermediate that upon loss of proton under basic conditions get transformed into another intermediate **4** (**Scheme 1**). The intermediate **4** subsequently underwent sulfonylation under reaction conditions resulting in thiazine derivatives **5** in reasonable yields (**Table 1**). The treatment of azatrienes **5** with equimolar ratio of methanesulfonyl chloride and triethylamine led to the incompletion of reaction with the partial generation of compound **5** (TLC based), clearly ruling out any possibility of compound **6** formed in the reaction. Moreover, the reaction did not proceed between **5** and methanesulfonyl chloride (TLC based) in the absence of triethylamine.

The detailed spectral features of the compounds **5** are given in the experimental section; however, the significant features are mentioned here. The compound **5a**, for example, analyzed for $C_{28}H_{29}NO_7S_2$, exhibited a molecular ion peak at *m/z* 555 (M^+) in its mass spectrum. The ^1H spectrum showed a characteristic doublet at δ 4.51 (*J* = 10.7 Hz) for one methine proton (H^1), one doublet of doublet (dd) at δ 4.76 (*J* = 10.7 Hz & 3.3 Hz) for another methine proton (H^2), a doublet at δ 5.75 (*J* = 3.3 Hz) for olefinic proton (H^3) and two doublets at δ 6.21 and 6.52 (*J* = 16.0 Hz) corresponding to two *trans* olefinic protons (H^4 & H^5) respectively. The characteristic four singlets at δ 2.97, 3.76, 3.82 and 3.83 confirmed the presence of single $-SO_2CH_3$ and three methoxy groups in the compound.

3. Conclusion

The highly regioselective cycloadditions reactions of azatrienes (**1)** with sulfene dienophile is described, and a series of new functionalized thiazine-dioxide scaffolds has been prepared. This is a first report, to the best of our knowledge, in which the [4 + 2] cycloadditions of 1-azabutadienes are explored with the sulfene dienophile.

4. Experimental Section

4.1. General

The cross-conjugated azatrienes **1** were prepared according to the reported procedure [19,20]. Thionyl chloride and methanesulfonyl chloride used were commercially available. Dichloromethane dried over *di*-phosphorus pentoxide and stored over molecular sieves (4 Å). Mass

Table 1. Reactions of azatrienes (1) with the sulfene.

S.No.	Compound	R	Ar	Yield (%)	M.P. (°C)
1	5a	-OCH_3	*p*-methoxyphenyl	79	113 - 114
2	5b	-OCH_3	*p*-tolyl	76	134 - 135
3	5c	-OCH_3	phenyl	69	121 - 122
4	5d	H	*p*-methoxyphenyl	77	118 - 119
5	5e	H	*p*-tolyl	68	125 - 126
6	5f	H	phenyl	71	130 - 131
7	5g	Cl	*p*-methoxyphenyl	75	136 - 137
8	5h	Cl	*p*-tolyl	72	132 - 133
9	5i	Cl	phenyl	78	116 - 117

spectra were recorded on Shimadzu GCMS-QP-2000 mass spectrometer. IR spectra were recorded on a Shimadzu D-8001 spectrophotometer. ^{1}H NMR spectra were recorded in deuterochloroform ($CDCl_3$) with Bruker AC-E 300 (300 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shift values are expressed as ppm downfield from TMS and *J* values are in Hz. Splitting patterns are indicated as s: singlet, d: doublet and dd: doublet of doublet. ^{13}C-NMR spectra were also recorded on AC-E 300 (75.0 MHz) spectrometer in a deuterochloroform ($CDCl_3$) using tetramethylsilane (TMS) as an internal standard. Melting points were determined by open capillary method using Veego Precision Digital Melting Point apparatus (MP-D) and are uncorrected. Elemental analyses were performed on Heraus CHN-O-Rapid Elemental Analyzer.

4.2. General Procedure for the Cycloaddition Reactions of Azatrienes (1) with Sulfene

To a well-stirred solution of azatrienes **1** (10 mmol) and triethylamine (30 mmol) in dry methylene chloride (30 mL) was added drop wise a solution of methanesulfonyl chloride (20 mmol) in dry methylene chloride (30 mL) over a period of 0.5 hour at 0˚C. After completion of the reaction (TLC), the reaction mixture was first washed with the saturated sodium bicarbonate solution (2 × 25 mL) and water (2 × 50 mL) and the organic layer dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (2:10, v/v).

6-Methanesulfonyl-2,5-*bis*-(4-methoxy-phenyl)-3-[2-(4-methoxy-phenyl)-vinyl]-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5a). Light yellow solid, yield 79%; mp 113˚C - 114˚C; IR (KBr) 1604, 1510, 1463 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$): δ 2.97 (s, 3H. -SO_2CH_3), 3.76 (s, 3H, -OCH_3), 3.82 (s, 3H, -OCH_3), 3.83 (s, 3H, -OCH_3), 4.51 (d, *J* = 10.7 Hz, 1H, H^1), 4.76 (dd, *J* = 10.7 & 3.3 Hz, 1H, H^2), 5.75 (d, *J* = 3.3 Hz, 1H, H^3), 6.21 (d, *J* = 16.0 Hz, 1H, H^4), 6.52 (d, *J* = 16.0 Hz, 1H, H^5), 6.78 (d, *J* = 8.6 Hz, 2H, ArH), 6.97 (d, *J* = 8.6 Hz, 2H, ArH), 7.15 (d, *J* = 8.6 Hz, 4H, ArH), 7.36 (d, *J* = 8.7 Hz, 2H, ArH), 7.44 (d, *J* = 8.7 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 43.1 (-CH), 44.1 (-SO_2CH_3), 55.2 (-OCH_3), 55.3 (-OCH_3), 55.4 (-OCH_3), 75.9 (-CH), 96.1, 114.0, 114.5, 119.7, 120.8, 127.8, 127.9, 128.5, 129.6, 130.1, 131.1, 132.6, 136.3, 159.2, 159.4, 159.8 ppm; MS (EI) *m/z*: 555 (M^+). Anal. Calcd. for $C_{28}H_{29}NO_7S_2$: C, 60.52; H, 5.26; N, 2.52%. Found: C, 60.71; H, 5.19; N, 2.47%.

6-Methanesulfonyl-5-(4-methoxy-phenyl)-3-[2-(4-methoxy-phenyl)-vinyl]-2-*p*-tolyl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5b). Colorless solid, yield 76%; mp 134˚C - 135˚C; IR (KBr) 1603, 1510, 1463 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$): δ 2.05 (s, 3H, -CH_3), 3.00 (s, 3H. -SO_2CH_3), 3.76 (s, 3H, -OCH_3), 3.83 (s, 3H, -OCH_3), 4.49 (d, *J* = 10.8 Hz, 1H, H^1), 4.75 (dd, *J* = 10.8 & 3.4 Hz, 1H, H^2), 5.77 (d, *J* = 3.4 Hz, 1H, H^3), 6.22 (d, *J* = 16.0 Hz, 1H, H^4), 6.50 (d, *J* = 16.0 Hz, 1H, H^5), 6.77 (d, *J* = 8.6 Hz, 2H, ArH), 6.96 (d, *J* = 8.6 Hz, 2H, ArH), 7.14 (d, *J* = 8.6 Hz, 2H, ArH), 7.23 - 7.43 (m, 6H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 21.0 (-CH_3), 43.2 (-CH), 44.2 (-SO_2CH_3), 55.3 (-OCH_3), 55.4 (-OCH_3), 76.1 (-CH), 96.1, 114.0, 114.6, 120.2, 120.8, 126.4, 127.9, 128.3, 128.5, 129.6, 132.7, 135.8, 136.3, 138.4, 159.5, 159.8 ppm; MS (EI) *m/z*: 539 (M^+). Anal. Calcd. for $C_{28}H_{29}NO_6S_2$: C, 62.32; H, 5.42; N, 2.60%. Found: C, 62.25; H, 5.51; N, 2.53%.

6-Methanesulfonyl-5-(4-methoxy-phenyl)-3-[2-(4-methoxy-phenyl)-vinyl]-2-phenyl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5c). Pale yellow solid, yield 69%; mp 121˚C - 122˚C; IR (KBr) 1604, 1510, 1462 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$): δ 2.99 (s, 3H. –SO_2CH_3), 3.79 (s, 3H, -OCH_3), 3.82 (s, 3H, -OCH_3), 4.47 (d, *J* = 10.8 Hz, 1H, H^1), 4.73 (dd, *J* = 10.8 & 3.3 Hz, 1H, H^2), 5.76 (d, *J* = 3.3 Hz, 1H, H^3), 6.21 (d, *J* = 16.0 Hz, 1H, H^4), 6.51 (d, *J* = 16.0 Hz, 1H, H^5), 6.79 (d, *J* = 8.6 Hz, 2H, ArH), 6.94 (d, *J* = 8.6 Hz, 2H, ArH), 7.11 - 7.46 (m, 9H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 42.9 (-CH), 44.1 (-SO_2CH_3), 55.1 (-OCH_3), 55.2 (-OCH_3), 76.0 (-CH), 96.1,

114.0, 114.3, 120.1, 121.2, 125.8, 127.4, 128.2, 129.3, 130.8, 132.1, 134.9, 135.8, 138.6, 159.2, 159.6 ppm; MS (EI) *m/z*: 525 (M^+). Anal. Calcd. for $C_{27}H_{27}NO_6S_2$: C, 61.69; H, 5.18; N, 2.66%. Found: C, 61.78; H, 5.11; N, 2.56%.

6-Methanesulfonyl-2-(4-methoxy-phenyl)-5-phenyl-3-styryl-5,6-dihydro-2H-[1,2]thiazine 1, 1-dioxide (5d). Yellow solid, yield 77%; mp 118˚C - 119˚C; IR (KBr) 1607, 1517, 1460 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 3.01 (s, 3H. $-SO_2CH_3$), 3.82 (s, 3H, $-OCH_3$), 4.57 (d, *J* = 10.5 Hz, 1H, H^1), 4.77 (dd, *J* = 10.5 & 2.9 Hz, 1H, H^2), 5.82 (d, *J* = 2.9 Hz, 1H, H^3), 6.34 (d, *J* = 16.0 Hz, 1H, H^4), 6.58 (d, *J* = 16.0 Hz, 1H, H^5), 6.85 (d, *J* = 8.5 Hz, 2H, ArH), 6.97 (d, *J* = 8.5 Hz, 2H, ArH), 7.22 - 7.44 (m, 10H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 42.7 (-CH), 43.8 ($-SO_2CH_3$), 55.4 ($-OCH_3$), 76.1 (-CH), 96.0, 113.8, 114.2, 119.9, 122.8, 125.4, 126.3, 128.1, 128.4, 130.2, 131.7, 132.8, 133.6, 135.9, 155.1, 159.8 ppm; MS (EI) *m/z*: 495 (M^+). Anal. Calcd. for $C_{26}H_{25}NO_5S_2$: C, 63.01; H, 5.08; N, 2.83%. Found: C, 62.94; H, 5.17; N, 2.76%.

6-Methanesulfonyl-5-phenyl-3-styryl-2-*p*-tolyl-5,6-dihydro-2H-[1,2]thiazine1,1-dioxide (5e). Colorless solid, yield 68%; mp 125˚C - 126˚C; IR (KBr) 1605, 1511, 1460 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 2.12 (s, 3H, $-CH_3$), 3.00 (s, 3H. $-SO_2CH_3$), 4.55 (d, *J* = 10.6 Hz, 1H, H^1), 4.74 (dd, *J* = 10.6 & 3.1 Hz, 1H, H^2), 5.82 (d, *J* = 3.1 Hz, 1H, H^3), 6.33 (d, *J* = 16.0 Hz, 1H, H^4), 6.54 (d, *J* = 16.0 Hz, 1H, H^5), 6.92 (d, *J* = 8.6 Hz, 2H, ArH), 7.10 (d, *J* = 8.6 Hz, 2H, ArH), 7.15 - 7.48 (m, 10H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 20.9 ($-CH_3$), 42.4 (-CH), 44.1 ($-SO_2CH_3$), 76.3 (-CH), 96.1, 114.1, 114.6, 120.4, 123.1, 124.9, 126.1, 128.6, 129.5, 130.2, 130.8, 131.6, 133.2, 133.9, 142.7, 159.5 ppm; MS (EI) *m/z*: 479 (M^+). Anal. Calcd. for $C_{26}H_{25}NO_4S_2$: C, 65.11; H, 5.25; N, 2.92%. Found: C, 65.23; H, 5.17; N, 2.86%.

6-Methanesulfonyl-2,5-diphenyl-3-styryl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5f). Colorless solid, yield 71%; mp 130˚C - 131˚C; IR (KBr) 1603, 1510, 1460 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 3.01 (s, 3H. $-SO_2CH_3$), 4.54 (d, *J* = 10.5 Hz, 1H, H^1), 4.71 (dd, *J* = 10.5 & 2.8 Hz, 1H, H^2), 5.82 (d, *J* = 2.8 Hz, 1H, H^3), 6.36 (d, *J* = 16.0 Hz, 1H, H^4), 6.53 (d, *J* = 16.0 Hz, 1H, H^5), 6.79 - 7.53 (m, 15H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 42.9 (-CH), 44.4 ($-SO_2CH_3$), 76.6 (-CH), 96.1, 114.0, 114.5, 120.6, 121.5, 122.5, 124.7, 126.7, 129.2, 130.5, 132.4, 133.4, 133.4, 135.7, 144.7, 159.6 ppm; MS (EI) *m/z*: 465 (M^+). Anal. Calcd. for $C_{25}H_{23}NO_4S_2$: C, 64.49; H, 4.98; N, 3.01%. Found: C, 64.59; H, 5.10; N, 2.96%.

5-(4-Chloro-phenyl)-3-[2-(4-chloro-phenyl)-vinyl]-6-methanesulfonyl-2-(4-methoxy-phenyl)-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5g). Yellow solid, yield 75%; mp 136˚C - 137˚C; IR (KBr) 1605, 1512, 1460 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 2.98 (s, 3H. $-SO_2CH_3$), 3.83 (s, 3H, $-OCH_3$), 4.55 (d, *J* = 10.5 Hz, 1H, H^1), 4.76 (dd, *J* = 10.5 & 3.2 Hz, 1H, H^2), 5.82 (d, *J* = 3.2 Hz, 1H, H^3), 6.38 (d, *J* = 16.0 Hz, 1H, H^4), 6.59 (d, *J* = 16.0 Hz, 1H, H^5), 6.83 (d, *J* = 8.7 Hz, 2H, ArH), 6.97 (d, *J* = 8.7 Hz, 2H, ArH), 6.99 - 7.45 (m, 8H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 42.6 (-CH), 43.9 ($-SO_2CH_3$), 55.4 ($-OCH_3$), 76.2 (-CH), 96.0, 114.1, 114.4, 120.3, 122.6, 125.3, 126.8, 127.8, 128.8, 129.5, 131.2, 131.9, 133.4, 135.2, 154.2, 159.6 ppm; MS (EI) *m/z*: 563 (M^+). Anal. Calcd. for $C_{26}H_{23}Cl_2NO_5S_2$: C, 55.32; H, 4.11; N, 2.48%. Found: C, 55.26; H, 4.22; N, 2.52%.

5-(4-Chloro-phenyl)-3-[2-(4-chloro-phenyl)-vinyl]-6-methanesulfonyl-2-*p*-tolyl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5h). Pale yellow solid, yield 72%; mp 132˚C - 133˚C; IR (KBr) 1603, 1510, 1460 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 2.21 (s, 3H, $-CH_3$), 3.01 (s, 3H. $-SO_2CH_3$), 4.53 (d, *J* = 10.5 Hz, 1H, H^1), 4.71 (dd, *J* = 10.5 & 3.1 Hz, 1H, H^2), 5.80 (d, *J* = 3.1 Hz, 1H, H^3), 6.36 (d, *J* = 16.0 Hz, 1H, H^4), 6.53 (d, *J* = 16.0 Hz, 1H, H^5), 6.90 (d, *J* = 8.7 Hz, 2H, ArH), 7.06 (d, *J* = 8.7 Hz, 2H, ArH), 7.13 - 7.49 (m, 8H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 21.0 ($-CH_3$), 42.6 (-CH), 44.4 ($-SO_2CH_3$), 76.6 (-CH), 96.0, 114.0, 114.3, 120.5, 123.4, 123.8, 125.4, 127.1, 127.8, 131.7, 131.9, 133.4, 133.9, 134.5, 142.5, 159.8 ppm; MS (EI) *m/z*: 547 (M^+). Anal. Calcd. for $C_{26}H_{23}Cl_2NO_4S_2$: C, 56.93; H, 4.23; N, 2.55%. Found: C, 57.03; H, 4.29; N, 2.61%.

5-(4-Chloro-phenyl)-3-[2-(4-chloro-phenyl)-vinyl]-6-methanesulfonyl-2-phenyl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5i): Colorless solid, yield 78%; mp 116˚C - 117˚C; IR (KBr) 1604, 1510, 1460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.99 (s, 3H. $-SO_2CH_3$), 4.51 (d, *J* = 10.4 Hz, 1H, H^1), 4.71 (dd, *J* = 10.4 & 3.1 Hz, 1H, H^2), 5.82 (d, *J* = 3.1 Hz, 1H, H^3), 6.33 (d, *J* = 16.0 Hz, 1H, H^4), 6.50 (d, *J* = 16.0 Hz, 1H, H^5), 6.69 - 7.49 (m, 15H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 43.0 (-CH), 44.9 ($-SO_2CH_3$), 76.8 (-CH), 96.0, 114.1, 114.3, 120.9, 122.2, 122.9, 123.8, 126.6, 129.2, 131.4, 132.3, 133.2, 133.6, 134.4, 143.1, 159.7 ppm; MS (EI) *m/z*: 533 (M^+). Anal. Calcd. for $C_{25}H_{21}Cl_2NO_4S_2$: C, 56.18; H, 3.96; N, 2.62%. Found: C, 56.26; H, 4.09; N, 2.53%.

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REFERENCES

[1] B. Groenendaal, E. Ruijter and R. V. A. Orru, "1-Azadienes in Cycloaddition and Multicomponent Reactions towards N-heterocycles," *Journal of Chemical Society, Chemical Communications*, No. 43, 2008, pp. 5474-5489. doi:10.1039/b809206k

[2] M. Behforouz and M. Ahmadian, "Diels-Alder Reactions of 1-Azadienes," *Tetrahedron*, Vol. 56, No. 30, 2000, pp. 5259-5288. doi:10.1016/S0040-4020(00)00259-3

[3] S. Jayakumar, M. P. S. Ishar and M. P. Mahajan, "Recent Advances in Synthetic Applications of Azadienes" *Tetrahedron*, Vol. 58, No. 3, 2002, pp. 379-471. doi:10.1016/S0040-4020(01)01050-X

[4] T. N. Danks and D. Velo-Rego, "Reaction of a Chromium Carbene Complex with 1-Azadienes and Synthesis of Trisubstituted Pyrroles," *Tetrahedron Letters*, Vol. 35, No. 50, 1994, pp. 9443-9444. doi:10.1016/S0040-4039(00)78565-0

[5] J. Barluenga, M. Tomas, J. A. Lopez-Pelegrin and E. Rubio, "Stereselective Cyclopropanation of 1-Azadienes with Fischer Carbine Complexes," *Journal of Chemical Society*, *Chemical Communications*, No. 6, 1995, pp. 665-666. doi:10.1039/c39950000665

[6] Y. N. Romaschin, M. T. H. Liu and R. J. Bonneau, "The Facile Synthesis of 1,2,3-Trisubstituted Pyrroles from the Reaction of Chlorocarbenes with 1-Azabuta-1,3-dienes," *Journal of Chemical Society*, *Chemical Communications*, No. 5, 1999, pp. 447-448. doi:10.1039/a809508f

[7] M. Chagr, H. Fillion and A. Pougny, "A Regioselective Synthesis of 4,5- and 4,8-Disubstitutedazaanthraquinones by the Diels-Alder Route," *Tetrahedron Letters*, Vol. 29, No. 46, 1988, pp. 5913-5916. doi:10.1016/S0040-4039(00)82224-8

[8] D. Berger and W. Imhof, "One-Pot Synthesis of γ-Lactams in a Reaction Cascade from α,β-Unsaturated Imines, CO and Ethylene Catalysed by $Ru_3(CO)_{12}$," *Journal of Chemical Society*, *Chemical Communications*, No. 16, 1999, pp. 1457-1458. doi:10.1039/a903266e

[9] J. Barluenga, I. Merino and S. Palacios, "One Pot Synthesis of 2-Vinyl-1-azadienes and Divinylketones," *Tetrahedron Letters*, Vol. 30, No. 40, 1989, pp. 5493-5496. doi:10.1016/S0040-4039(01)80602-X

[10] N. Martin, A. M. Grau, L. Sanchez, C. Seoane and M. Torres, "The First Hetero-Diels-Alder Reaction of 60˚C with 1-Azadienes. Synthesis of Tetrahydropyrido [2',3': 1,2][60]fullerene Derivatives," *Journal of Organic Chemistry*, Vol. 63, No. 22, 1998, pp. 8074-8076.

[11] C. R. Berry and R. P. Hsung, "Inverse Electron-Demand Aza-[4 + 2] Cycloaddition Reactions of Allenamides," *Tetrahedron*, Vol. 60, No. 35, 2004, pp. 7629-7636. doi:10.1016/j.tet.2004.05.117

[12] R. C. Clark, S. Pfeiffer and D. L. Boger, "Diastereoselective Diels-Alder Reactions of N-Sulfonyl- 1-aza-1,3-butadienes with Optically Active Enol Ethers: An Asymmetric Variant of the 1-Azadiene Diels-Alder Reaction," *Journal of American Chemical Society*, Vol. 128, No, 8, 2006, pp. 2587-2593. doi:10.1021/ja0571646

[13] M. He, R. Struble and J. W. Bode, "Highly Enantioselective Azadiene Diels-Alder Reactions Catalyzed by Chiral N-Heterocyclic Carbenes," *Journal of American Chemical Society*, Vol. 128, No. 26, 2006, pp. 8418-8420. doi:10.1021/ja062707c

[14] A. Robin, K. Julienne, J. C. Meslin and D. Deniaud, "Synthesis of Pyridone and Pyridine Rings by [4 + 2] Hetero-Cyclocondensation," *Tetrahedron Letters*, Vol. 45, No. 52, 2004, pp. 9557-9559. doi:10.1016/j.tetlet.2004.10.142

[15] M. C. Elliott, E. Kruiswijk and D. J. Willock, "Asymmetric Hetero-Diels-Alder Reactions. Reactions of Oxazolo [3,2-c]pyrimidines," *Tetrahedron*, Vol. 57, No. 51, 2001, pp. 10139-10146. doi:10.1016/S0040-4020(01)01032-8

[16] D. L. Boger, "Diels-Alder Reactions of Azdienes," *Tetrahedron*, Vol. 39, No. 18, 1983, pp. 2869-2939. doi:10.1016/S0040-4020(01)92154-4

[17] D. L. Boger and S. M. Weinreb, "In Hetero Diels-Alder Methodology in Organic Synthesis," Academic Press Inc., San Diego, 1987, p 239.

[18] S. N. Mazumdar, M. Sharma and M. P. Mahajan, "Diels-Alder Cycloaddition Reactions of 1,3-Diazabutadienes with Sulfene," *Tetrahedron Letters*, Vol. 28, No. 23, 1987, pp. 2641-2642. doi:10.1016/S0040-4039(00)96169-0

[19] P. Singh, G. Bhargava and M. P. Mahajan, "Tandem [2 + 2] Cycloaddition and Cope Rearrangement in Reactions of Cross-Conjugated Azatrienes with Conjugated Ketenes: A Facile Single Step Synthesis of Novel Azocinone Derivatives," *Tetrahedron*, Vol. 62, No. 48, 2006, pp. 11267-11273. doi:10.1016/j.tet.2006.09.007

[20] M. H. Elnagdi, S. M. Mousawi, M. M. Abdel-Khalik, S. El-Sheriny and E. John, "Studies with Enaminones: Reactivity of 1,5-Disubstituted-1,4-pentadien-3-ones toward Electrophilic Reagents. A Novel Route to Azolylazines, Benzofuranals, Pyranones," *Journal of Heterocyclic Chemistry*, Vol. 38, No. 4, 2001, pp. 949-953. doi:10.1002/jhet.5570380422

