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Effect of solvent nature on the regioselectivity of the reactions of pyridinium ylides with *E*-1,2-di(alkylsulfonyl)-1,2-dichloroethene. From the reaction of 1,3-dipolar cycloaddition to the reaction of nucleophilic addition–elimination (Ad_N–$E_{1,5}$)

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ABSTRACT

The effect of solvent nature on the reactions of pyridinium ylides with *E*-1,2-di(alkylsulfonyl)-1,2-dichloroethene was investigated for the first time. It was found, that in aprotic solvents ($CHCl_3$, DMF, CH_3CN) these reactions take place as a 1,3-dipolar cycloaddition (1,3-DC) followed by double elimination with the formation of substituted 1,2-di(alkylsulfonyl)indolizines. In a protic solvent (EtOH) in the presence of excess Et_3N and heating, the reactions of substituted pyridinium salts with *E*-1,2-di(alkylsulfonyl)-1,2-dichloroethenes take place simultaneously as a 1,3-DC and as an addition–elimination (Ad_N–$E_{1,5}$) and lead to the formation of 1,2-di(alkylsulfonyl)indolizines and 4,5-di(alkylsulfonyl) furans.

1. Introduction

1,3-Dipolar cycloaddition reactions of pyridinium ylides, quinolinium ylides, and isoquinolinium ylides with unsaturated compounds have been widely used in the preparative synthesis of indolizines, imidazopyridines, and other cycloazines.[1–5] The influence of the structures of the azinium ylides and of the unsaturated compounds on the regio- and stereoselectivity of these reactions is well known. Usually, for the synthesis of aromatic indolizines, reactions of pyridinium ylides with acetylenes are used.[1–5] As a rule, reactions of azinium ylides with π-deficient ethylenes proceed stereoselectively with the formation of hydrogenated indolizines.[6–8] The reactions of unsaturated nitriles with pyridinium ylides lead to the formation of cyclopropanes.[7,10] Reduction of the electron density in the azinium ylide leads to a change in the direction of reactions of azinium ylides with unsaturated nitriles. For example, the reactions of unsaturated nitriles with 3-cyanopyridinium ylides or isoquinolinium ylides form tetrahydroindolizines or tetrahydrobenzoindolizines, respectively.[11–13]

In the presence of electrophilic groups, such as fluoride or chloride in a π-deficient ethylene, the 1,3-dipolar cycloaddition reaction is followed by an elimination reaction to form aromatic indolizines.[14–17]

Depending on the temperature conditions and the structures of the pyridinium ylides, their reactions with unsaturated compounds can proceed as double cycloadditions. For example, the reaction of the acetylenedicarboxylic acid dimethyl ester with a pyridinium ylide leads to a mixture of indolizine and quinazoline.[3]

Consequently, the dependence of regio- and stereoselectivity of reactions of azinium ylides with unsaturated compounds on the structure of the starting compounds and temperature is well known. To date, the effect of the solvent nature on these reactions remains virtually unexplored.[1–5]

2. Results and discussion

Investigating the reactions of pyridinium ylides **2** with *E*-1,2-di(alkylsulfonyl)-1,2-dichloroethenes **3**, we first discovered that

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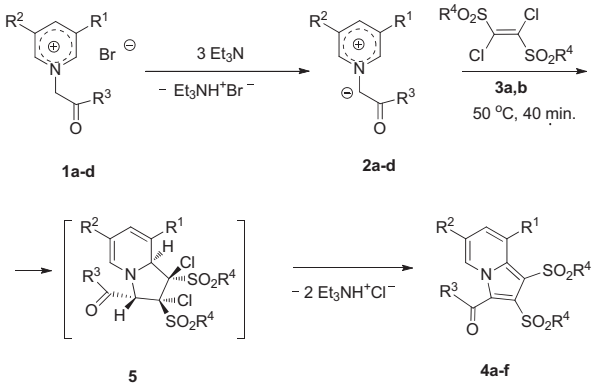
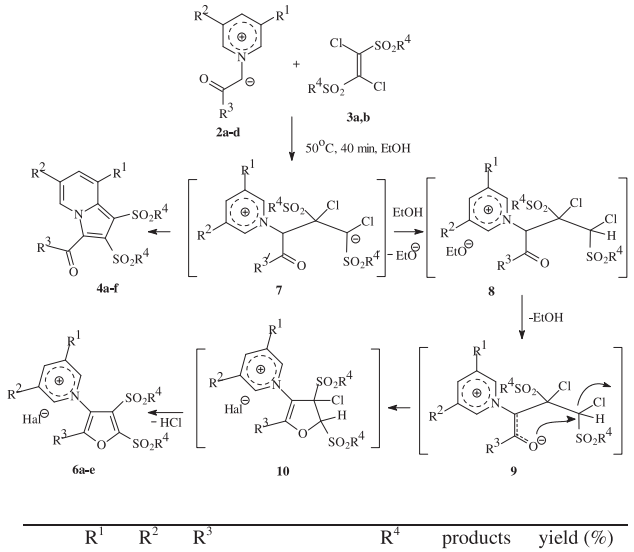
the solvent nature significantly affects the regioselectivity of such reactions. Pyridinium salts **1** were treated with Et_3N in a solvent, generating pyridinium ylides **2**, followed by the addition of ethenes **3**. The reaction mixture was heated up to 50 °C for 40 min. We found that the reactions of pyridinium ylides **2a**–**d** with ethenes **3a**,**b** in $CHCl_3$ in the presence of Et_3N proceed regioselectively with the formation of a high yield of substituted 1,2-di(alkylsulfonyl) indolizines **4a**–**f** (65–73%) (Scheme 1). In polar aprotic solvents (CH_3CN or DMF) the reactions of pyridinium ylide **2a** with ethene **3a** also occur with the formation of indolizine **4a** (62 or 64%, respectively). The formation of indolizines **4** can be represented with a classical scheme of the 1,3-dipolar cycloaddition reaction through the adduct **5**. Subsequent double dehydrochlorination of **5** leads to the aromatic indolizines **4**.



	R^1	R^2	R^3		R^4	Solvent	Product	Yield (%)
2a	H	H	2,4-Me_2-C_6H_3	**3a**	Et	$CHCl_3$	**4a**	73
2a	H	H	2,4-Me_2-C_6H_3	**3a**	Et	MeCN	**4a**	62
2a	H	H	2,4-Me_2-C_6H_3	**3a**	Et	DMF	**4a**	64
2a	H	H	2,4-Me_2-C_6H_3	**3b**	n-Pr	$CHCl_3$	**4b**	69
2b	Me	Me	2,4-Me_2-C_6H_3	**3b**	n-Pr	$CHCl_3$	**4c**	75
2c	Me	Me	4-F-C_6H_4	**3b**	n-Pr	$CHCl_3$	**4d**	67
2d	Me	H	2,4-Me_2-C_6H_3	**3b**	n-Pr	$CHCl_3$	**4e** + **4f**[a]	65

[a] A mixture of substituted 6-methyl- **4e** and 8-methylindolizines **4f** was isolated.

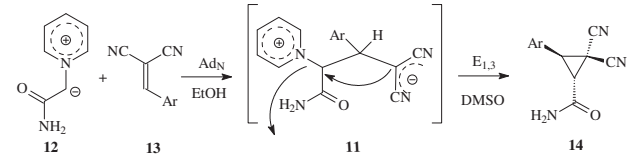
Scheme 1. The reactions of pyridinium ylides **2a**–**d** with ethenes **3a**,**b** in aprotic solvents.



	R^1	R^2	R^3		R^4	products		yield (%)	
						6[a]		**6**[a]	**4**
2a	H	H	2,4-Me_2-C_6H_3	**3a**	Et	**6a**	**4a**	38	14
2a	H	H	2,4-Me_2-C_6H_3	**3a**	n-Pr	**6b**	**4b**	36	17
2b	Me	Me	2,4-Me_2-C_6H_3	**3b**	n-Pr	**6c**	**4c**	50	9
2c	Me	Me	4-F-C_6H_4	**3b**	n-Pr	**6d**	**4d**	12	44
2d	Me	H	2,4-Me_2-C_6H_3	**3b**	n-Pr	**6e**	**4e** + **4f**	38	18

[a] Furans **6a-e** were isolated as a mixture of substituted 1-[2-Phenyl-4,5-bis(alkylsulfonyl)-3-furyl]pyridinium bromides and chlorides. Br^- ions were present in the reaction medium because pyridinium ylides **2** were generated in situ, by treatment of phenacylpyridinium bromides with Et_3N. The yields of pyridinium bromides are shown. Resulting mixtures of pyridinium halides **6a-e** were converted into bromides by heating them with an excess of HBr.

Scheme 2. The reactions of pyridinium ylides **2a**–**d** with ethenes **3a**,**b** in EtOH.



Scheme 3. The reactions of pyridinium ylides and arylidenmalononitriles in alcohol.

In a protic solvent (EtOH) reactions of pyridinium ylides **2a**–**d** with ethenes **3a**,**b** proceed with the formation of a mixture of substituted 1,2-di(alkylsulfonyl)furans **6a**–**e** and the corresponding indolizines **4a**–**f** as minor components (Scheme 2). Formation of an indolizine ring can probably occur not only simultaneously through the adduct of 1,3-DC **5**, but also stepwise. In this case, a Michael adduct (reaction Ad_N) in the form of a zwitterion **7** is formed initially. Subsequent intramolecular closure of zwitterion **7** and double elimination of HCl leads to the formation of indolizines **4**. However, the dominant direction of the reaction, presumably, begins with the stage of protonation of the zwitterion **7** with ethanol and the formation of adduct **8**. The adduct **8** gets deprotonated with EtO^- under the reaction conditions with the formation of enolate **9**. 1,5-Elimination of HCl leads to the closure of the dihydrofuran ring **10**, subsequent 1,2-elimination of HCl leads to substituted furan **6**. Furans **6** were isolated and characterized as salts.

Note, that similar zwitterions **11** were isolated from the reactions of pyridinium ylides **12** and arylidenmalononitriles **13** in alcohol (Scheme 3).[9,10] However, they underwent 1,3-elimination in EtOH or DMSO with the formation of cyclopropanes.[14] A cyclization reaction to give the corresponding indolizine was not observed.

Furans **6a**–**e** were isolated as a mixture of substituted 1-[2-phenyl-4,5-bis(alkylsulfonyl)-3-furyl]pyridinium bromides and chlorides in a ratio of approximately 8:1 (The ratios were calculated based on the results of potentiometric titration of a mixture of halides with 0.01 N solution of $AgNO_3$). The resulting mixtures of pyridinium halides **3a**–**e** were converted in to bromides by heating them with an excess of HBr.

The structures of the synthesized compounds **4** and **6** were confirmed by elemental analysis, ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectrometry. The IR spectra of the compounds **4** and **6** contain absorption bands corresponding to the stretching vibrations of the sulfonyl group[18] at 1332–1312 and 1148–1140 cm^{-1}. In addition, the spectra of indolizines **4** contain characteristic bands for the carbonyl group absorption corresponding to the stretching vibrations in the region 1672–1664 cm^{-1}. In the mass spectra of all synthesized indolizines **4a**–**f** the molecular ions M^+ were present. In the case of furans **6a**–**e**, signals corresponding to the mass of the cations $[M-Br]^+$ were present. In the ^1H NMR spectra of furans **6** proton signals of the pyridine fragment are found in the lower fields relative to the signals of the corresponding protons in the indolizines **4**. The signals of H(2) and H(6) in the furans **6** appear as two doublets in **6a**,**b**,

a singlet and a doublet in **6e**, and a singlet in **6d**,**e** in the area 9.25–9.55 ppm. The H(5) proton in the indolizines **4** shows as a doublet in **4a**,**b** and a singlet in **4c**,**d** in the area 7.84–8.40 ppm. In the reaction of ethene **1b** with ylide **2d**, an isomeric mixture of substituted 6-methyl **4e** and 8-methylindolizine **4f** along with furan **6e** was isolated. This mixture had a ratio between **4e** and **4f** of 1:2 based on an analysis of the ^{1}H NMR spectrum. Previously, we reported the formation of two isomeric indolizines in the reaction of *E*-1,2-di(alkylsulfonyl)-1,2-dichloroethene with β-picolinium ylide.[16]

The structure of furan **6c** was investigated by X-ray analysis (Fig. 1). Geometric parameters of the cation have usual values.[19] The **s**ubstituted furan heterocycle is strictly flat (deviation from the mean plane of atoms does not exceed 0.002 Å). Steric hindrance due to the presence of many shortened intramolecular non-valence contacts influences the geometry of the propylsulfonyl substituents and causes the turning of the 3,5-dimethylpyridine and 2,4-dimethylphenyl substituents relative to the plane of the heterocycle ring at 85.6° and 33.2°, respectively. The dihedral angle between 3,5-dimethylpyridine and 2,4-dimethylphenyl substituents is equal to 88.9°. There are distortions from the tetrahedral configuration observed at sulfur atoms, such that angles range between 103.2(3) ° and 119.4(3)° at atom S(1) and between 104.4(3)° and 119.2(3)° at atom S(2). These values are usual for substituted arylsulfones,[20] and coincide with the values found in earlier work in the substituted 1,2-di(ethylsulfonyl)indolizine.[15]

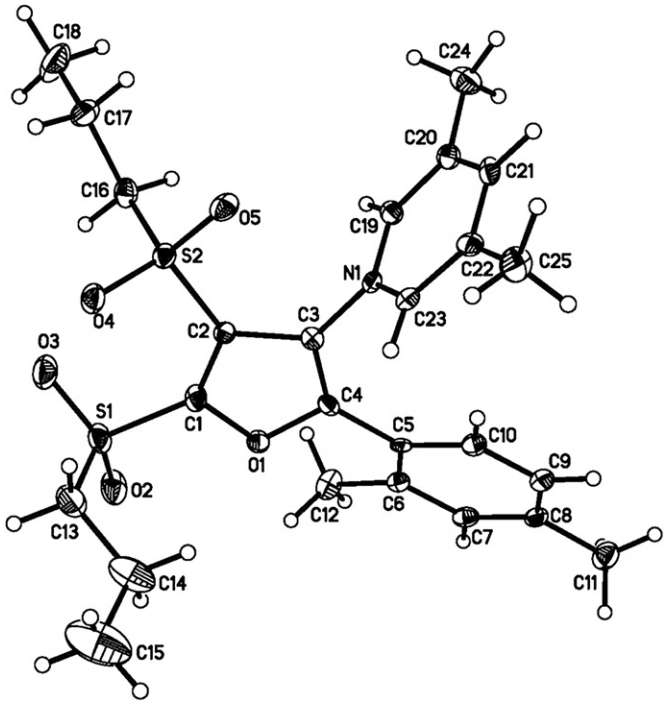


Fig. 1. X-ray structure of compound **6c**. Ellipsoids were drawn at the 50% level.

3. Conclusion

We were the first to observe the effect of the solvent nature on the reaction of pyridinium ylides with *E*-1,2-di(alkylsulfonyl)-1,2-dichloroethenes. It was found, that in aprotic solvents ($CHCl_3$, DMF, CH_3CN) this reaction proceeds as a 1,3-dipolar cycloaddition (1,3-DC) followed by double elimination with the formation of substituted 1,2-di(alkylsulfonyl)indolizines. In a protic solvent (EtOH), the reaction of substituted pyridinium ylides with *E*-1,2-di(alkylsulfonyl)-1,2-dichloroethenes occurs simultaneously as a 1,3-DC and as an addition–elimination (Ad_N–$E_{1,5}$) and leads to the formation of 1,2-di(alkylsulfonyl)indolizines and 4,5-di(alkylsulfonyl) furans.

4. Experimental section

4.1. General

All synthesized compounds were characterized by elemental microanalysis, ^{1}H, ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectrometry. The progress of reactions and the compounds' purity were monitored by thin layer chromatography on silica gel-coated aluminum plates with the use of a 2:1 hexane/acetone mixture as an eluent and visualized under a UV lamp (254 nm). Melting points were measured on a Kofler stage and are uncorrected. Elemental microanalyses were obtained on a Perkin–Elmer 2400 CHN analyzer. The analytical results for C, H, and N were within ±0.4 of the theoretical values. The IR spectra of the compounds were recorded on Perkin–Elmer-577 Specord M-82 Fourier-spectrometer in KBr pellets (1:200 mass), the frequencies are expressed in cm^{-1}. The ^{1}H NMR spectra were recorded on Bruker DRX-500 (500 MHz), Bruker AH-300 (300 MHz), and Bruker WM-250 (250 MHz) and ^{13}C NMR spectra were recorded on Bruker AM-300 (75.47 MHz) instruments for 5–12% solutions in DMSO-d_6 with TMS as an internal standard and $CDCl_3$. Chemical shift values are listed in parts per million (ppm) with reference to DMSO-d_6 (^{1}H, 2.50; ^{13}C, 39.50) or $CDCl_3$ (^{1}H, 7.25, ^{13}C, 77.0). Coupling constants (*J*) are given in Hertz. Hydrogen multiplicity (C, CH, CH_2, CH_3) information of ^{13}C NMR spectra was obtained from carbon JMOD-XH technique. The mass spectra of indolizines **4a**–**f** and furans **6a**–**e** were obtained on a FINNIGAN MAT INCOS 50 quadrupole mass spectrometer with ionization energy of 70 eV. High-resolution mass spectrometry data for pyridinium salts **1a**–**d** were acquired using a Q-TOF analyzer in CH_3CN as solvent.

4.2. Pyridinium salts 1a–d

Compounds **1a**–**d** were obtained from commercially available pyridines by alkylation with the corresponding phenacyl bromides at dry acetone on reflux.[21]

4.2.1. 1-[2-(2,4-Dimethylphenyl)-2-oxoethyl]pyridinium bromide ***1a***. Yield=92%, a white solid with mp 214–215 °C (lit. 211.5–212.5 °C).[22] IR: 2923, 1680 cm^{-1}. ^{1}H NMR (DMSO-d_6, 300 MHz) *δ*: 2.39 (s, 3H, 4-*Me* Ph), 2.46 (s, 3H, 2-*Me* Ph), 6.50 (s, 2H, CH_2CO), 7.26 (s, 1H, *3-H* Ph), 7.32 (d, 1H, *J* 8.0 Hz, *5-H* Ph), 8.00 (d, 1H, *J* 8.0 Hz, *6-H* Ph), 8.29 (t, 2H, *J* 7.0 Hz, *3-H*, *5-H* Py), 8.77 (t, 1H, *J* 7.8 Hz, *4-H* Py), 9.08 (d, 2H, *J* 6.1 Hz, *2-H*, *6-H* Py). ^{13}C NMR (DMSO-d_6, 75.47 MHz) *δ*: 21.0, 21.3, 67.2, 126.7, 127.7 (3C), 130.1, 130.2, 132.9, 139.5, 143.7 (2C), 146.2, 192.0. Anal. Calcd for $C_{15}H_{16}BrNO$: C, 58.84; H, 5.27; N, 4.57. Found: C, 59.05; H, 5.35, N, 4.50.

4.2.2. 1-[2-(2,4-Dimethylphenyl)-2-oxoethyl]-3,5-dimethylpyridinium bromide ***1b***. Yield=85%, a white solid with mp 219–220 °C. IR: 2928, 1684 cm^{-1}. ^{1}H NMR (DMSO-d_6, 300 MHz) *δ*: 2.38 (s, 3H, *4-Me* Ph), 2.46 (s, 3H, *2-Me* Ph), 2.49 (s, 6H, *3-Me*, *5-Me* Py), 6.35 (s, 2H, CH_2CO), 7.20-7.38 (m, 2H, *5-H*, *6-H* Ph), 8.00 (s, 1H, *3-H* Ph), 8.35 (s, 1H, *4-H* Py), 8.85 (s, 2H, *2-H*, *6-H* Py). ^{13}C NMR (DMSO-d_6, 75.47 MHz) *δ*: 17.7, 21.0, 21.3, 66.7, 126.7, 130.1, 130.3, 132.9, 137.3, 139.3, 143.0, 143.6, 146.9, 192.1. MS *m*/*z* 254.155 (M^+–Br). Anal. Calcd for $C_{17}H_{20}BrNO$: C, 61.09; H, 6.03; N, 4.19. Found: C, 61.33; H, 6.10; N, 4.27.

4.2.3. 1-[2-(3-Fluorophenyl)-2-oxoethyl]-3,5-dimethylpyridinium bromide ***1c***. Yield=83%, a white solid with mp 196–197 °C. IR: 3013, 1696 cm^{-1}. ^{1}H NMR (DMSO-d_6, 300 MHz) *δ*: 2.50 (s, 6H, *3-Me*, *5-Me* Py), 6.48 (s, 2H, CH_2CO), 7.52 (t, 2H, *J* 8.8 Hz, *3-H*, *5-H* Ph), 8.14–8.21 (m. 2H, *2-H*, *4-H Ph*), 8.45 (s, 1H, *4-H* Py), 8.80 (s, 2H, *2-H*, *6-H* Py). ^{13}C

NMR (DMSO-d_6, 75.47 MHz) δ: 17.7 (3-Me, 5-Me Py), 65.7, 116.1, 116.4, 130.3 (3-C, 5-C Py), 131.4, 131.5, 137.5, 143.0 (2C), 147.1, 164.0, 167.4, 189.5. MS m/z 244.114 (M^+–Br). Anal. Calcd for $C_{15}H_{15}BrFNO$: C, 55.60; H, 4.67; N, 4.32. Found: C, 55.83; H, 4.76; N, 4.24.

4.2.4. 1-[2-(2,4-Dimethylphenyl)-2-oxoethyl]-3-methylpyridinium bromide ***1d***. Yield=91%, a white solid with mp 210–211 °C. IR: 2925, 1681 cm^{-1}. ^1H NMR (DMSO-d_6, 300 MHz) δ: 2.38 (s, 3H, *4-Me* Ph), 2.47 (s, 3H, *2-Me* Ph), 2.55 (s, 3H, *3-Me* Py), 6.45 (s, 2H, CH_2CO), 7.25 (s, 1H, *3-H* Ph), 7.30 (d, 1H, *J* 8.1 Hz, *5-H* Ph), 8.03 (d, 1H, *J* 8.0 Hz, *6-H* Ph), 8.18 (t, 1H, *J* 7.0 Hz, *5-H* Py), 8.59 (d, 1H, *J* 7.8 Hz, *4-H* Py), 8.93 (d, 1H, *J* 5.6 Hz, *6-H* Py), 9.00 (s, 1H, *2-H* Py). ^{13}C NMR (DMSO-d_6, 75.47 MHz) δ: 17.8 (CH_3), 21.0 (CH_3), 21.2 (CH_3), 66.9 (CH_2), 126.7 (CH), 127.0 (CH), 130.0 (CH), 130.2 (C), 132.9 (CH), 138.1 (C), 139.4 (C), 143.5 (C), 143.7 (CH), 145.5 (CH), 146.5 (CH), 192.0 (C). MS m/z 240.138 (M^+–Br). Anal. Calcd for $C_{16}H_{18}BrNO$: C, 60.04; H, 5.67; N, 4.37. Found: C, 60.28; H, 5.71; N, 4.30.

4.3. *E*-1,2-Di(alkylsulfonyl)-1,2-dichloroethenes 3a,b

Compounds **3a**,**b** were synthesized according to a procedure described earlier.[18]

4.4. Substituted 1,2-di(alkylsulfonyl)indolizines 4a–f (general procedure)

Triethylamine (3 mmol) was added to a stirred solution of pyridinium salt **1** (1 mmol) in 8 ml of $CHCl_3$ (CH_3CN, DMSO) and then a solution of sulfone **3** (1 mmol) was added dropwise. The reaction mixture was heated at 50 °C for 40 min (progress monitored by thin layer chromatography), diluted with $CHCl_3$, washed with water, and dried with $MgSO_4$. The solvent was evaporated and the solid residue was recrystallized (Et_2O/$CHCl_3$=1:2).

4.4.1. [1,2-Bis(Ethylsulfonyl)-3-indolizinyl](2,4-dimethylphenyl) methanone ***4a***. Yield=0.32 g (73%) a white solid with mp 153–154 °C. IR: 1668, 1312, 1136 cm^{-1}. ^1H NMR (DMSO-d_6, 300 MHz) δ: 1.00 (t, 3H, *J* 7.3 Hz, CH_3CH_2), 1.20 (t, 3H, *J* 7.3 Hz, CH_3CH_2), 2.34 (s, 3H, *4-*CH_3 Ph), 2.58 (s, 3H, *2-*CH_3 Ph), 3.42–3.56 (m, 4H, 2CH_2SO_2), 7.05–7.11 (m, 2H, *C(7)H*, *5-H* Ph), 7.24–7.26 (m, 2H, *C(6)H*, *3-H* Ph), 7.44–7.49 (m, 1H, *C(8)H*), 8.13 (d, 1H, *J* 7.3 Hz, *6-H* Ph), 8.23 (d, 1H, *J* 9.5 Hz, *C(5)H*). ^{13}C NMR (DMSO-d_6, 75.47 MHz) δ: 6.0 (CH_3), 7.0 (CH_3), 20.8 (CH_3), 21.0 (CH_3), 50.5 (CH_2), 51.3 (CH_2), 105.9 (C), 116.1 (CH), 118.6 (CH), 124.5 (C), 125.4 (CH), 126.5 (CH), 126.8 (CH), 128.8 (C), 131.9 (CH), 132.8 (CH), 133.8 (C), 135.9 (C), 140.1 (C), 144.0 (C), 188.2 (C). MS m/z 433 (M^+, 23). Anal. Calcd for $C_{21}H_{23}NO_5S_2$: C, 58.18; H, 5.35; N, 3.23. Found: C, 58.37; H, 5.41; N, 3.30.

4.4.2. [1,2-Bis(Propylsulfonyl)-3-indolizinyl](2,4-dimethylphenyl) methanone ***4b***. Yield=0.32 g (69%) a white solid with mp 122–123 °C. IR: 1664, 1304, 1144 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ: 0.88 (t, 3H, *J* 7.2 Hz, CH_3CH_2), 1.02 (t, 3H, *J* 7.2 Hz, CH_3CH_2), 1.57–1.70 (m, 2H, CH_3CH_2), 1.72–1.88 (m, 2H, CH_3CH_2), 2.37 (s, 3H, *4-*CH_3 Ph), 2.66 (s, 3H, *2-*CH_3 Ph), 3.30–3.60 (m, 4H, 2CH_2SO_2), 6.87–6.93 (m, 1H, *C(7)H*), 6.98 (d, 1H, *J* 7.8 Hz, *5-H* Ph), 7.06 (d, 1H, *J* 7.8 Hz, *6-H* Ph), 7.19 (s, 1H, *3-H* Ph), 7.23–7.30 (m, 1H, *C(6)H*), 7.98 (d, 1H, *J* 7.3 Hz, *C(8)H*), 8.40 (d, 1H, *J* 9.1 Hz, *C(5)H*). ^{13}C NMR (DMSO-d_6, 75.47 MHz) δ: 12.5 (CH_3), 12.5 (CH_3), 14.9 (CH_2), 15.9 (CH_2), 20.7 (CH_3), 21.0 (CH_3), 57.4 (CH_2), 58.5 (CH_2), 106.7 (C), 116.2 (CH), 118.6 (CH), 125.4 (CH), 126.4 (CH), 126.8 (CH), 128.4 (C), 131.7 (CH), 132.7 (2CH), 134.1 (C), 135.7 (C), 140.0 (C), 143.9 (C), 188.2 (C). MS m/z 461 (M^+, 15). Anal. Calcd for $C_{23}H_{27}NO_5S_2$: C, 59.85; H, 5.90; N, 3.03. Found: C, 60.12; H, 5.97; N, 2.96.

4.4.3. [6,8-Dimethyl-1,2-bis(propylsulfonyl)-3-indolizinyl](2,4-dimethylphenyl) methanone ***4c***. Yield=0.37 g (75%) a white solid with mp 175–176 °C. IR: 1664, 1304, 1140 cm^{-1}. ^1H NMR (DMSO-d_6, 300 MHz) δ: 0.77 (t, 3H, *J* 7.4 Hz, CH_3CH_2), 1.04 (t, 3H, *J* 7.4 Hz, CH_3CH_2), 1.33–1.60 (m, 2H, CH_3CH_2), 1.77–1.92 (m, 2H, CH_3CH_2), 2.20 (s, 3H, *6-Me* Ind.), 2.34 (s, 3H, *4-Me* Ph), 2.57 (s, 3H, *2-Me* Ph), 2.72 (s, 3H, 8-*Me* Ind.), 3.30–3.42 (m, 2H, CH_2SO_2), 3.55–3.62 (m, 2H, CH_2SO_2), 7.07 (d, 1H, *J* 7.4 Hz, *5-H* Ph), 7.14 (d, 1H, *J* 8.1 Hz, *6-H* Ph), 7.20 (s, 1H, *3-H* Ph), 7.25 (s, 1H, *C(7)H*), 7.84 (s, 1H, *C(5)H*). ^{13}C NMR (DMSO-d_6, 75.47 MHz) δ: 12.6, 12.8, 15.0, 15.3, 17.1, 20.7, 21.0, 22.1, 57.7, 69.3, 110.4, 120.6, 125.2, 126.4, 127.6, 128.5, 128.7, 131.5, 132.2, 132.7, 133.3, 134.3, 140.0, 143.6, 189.3. MS m/z 489 (M^+, 19). Anal. Calcd for $C_{25}H_{31}NO_5S_2$: C, 61.32; H, 6.38; N, 2.86. Found: C, 61.59; H, 6.44; N, 2.85.

4.4.4. [6,8-Dimethyl-1,2-bis(propylsulfonyl)-3-indolizinyl](4-fluorophenyl) methanone ***4d***. Yield=0.32 g (67%), an yellow solid with mp 155–156 °C. IR: 1700, 1324, 1140 cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz) δ: 0.86 (t, 3H, *J* 7.44 Hz, CH_3CH_2), 1.04 (t, 3H, *J* 7.44 Hz, CH_3CH_2), 1.52–1.59 (m, 2H, CH_3CH_2), 1.82–1.90 (m, 2H, CH_3CH_2), 2.16 (s, 3H, *6-Me* Ind.), 2.70 (s, 3H, *8-Me* Ind.), 3.57–3.61 (m, 4H, 2CH_2SO_2), 7.20 (s, 1H. *C(7)H*), 7.37–7.41 (m, 2H, *3-H*, *5-H* Ph), 7.73 (s, 1H, *C(5)H*), 7.82–7.85 (m, 2H, *2-H*, *6-H* Ph). ^{13}C NMR (DMSO-d_6, 75.47 MHz) δ: 12.6 (CH_3), 12.8 (CH_3), 15.3 (CH_2), 15.4 (CH_2), 16.9 (CH_3), 22.1 (CH_3), 58.0 (CH_2), 59.5 (CH_2), 110.3 (C), 116.0 (CH), 116.3 (CH), 120.6 (CH), 125.3 (C), 126.8 (C), 128.6 (C), 131.9 (CH), 132.2 (CH), 132.3 (CH), 133.5 (C), 133.7 (C), 164.0 (C), 167.3 (C), 186.5 (C). MS m/z 479 (M^+, 21). Anal. Calcd for $C_{23}H_{26}FNO_5S_2$: C, 57.60; H, 5.46; N, 2.92. Found: C, 57.32; H, 5.51; N, 2.88.

4.4.5. (2,4-Dimethylphenyl)[6-methyl-1,2-bis(propylsulfonyl)-3-indolizinyl] methanone ***4e*** *and (2,4-dimethylphenyl)[8-methyl-1,2-bis(propyl-sulfonyl)-3-indolizinyl]methanone* ***4f***. Yield=0.31 g (65%) a white solid IR: 1664, 1324, 1140 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ: 0.87 (t, 3H, *J*=7.3 Hz, CH_3CH_2 **4e**), 0.98–1.21 (m, CH_3CH_2 **4e,** 2CH_3CH_2 **4f**), 1.52–1.71 (m, 2H, CH_3CH_2 **4e**,**f**), 1.75–2.11 (m, 2H, CH_3CH_2 **4e**,**f**), 2.26 (s, 6-*Me* Ind.**4e**), 2.37 (s, 3H, *4-Me* Ph **4e,f**), 2.66 (s, 3H, *2-Me* Ph **4e**,**f**), 2.80 (s, *8-Me* Ind. **4f**), 3.29–3.68 (m, 4H, 2CH_2SO_2 **4e**,**f**), 6.73–6.82 (m, *C(6)H* **4f**), 6.96 (d, 1H, *J* 7.9 Hz, *5-H* Ph **4e**,**f**), 7.03 (d, 1H, *J*=7.3 Hz, *6-H* Ph **4e**,**f**), 7.08–7.14 (m, *C(7)H* **4e**, *C(7)H* **4f**), 7.18 (s, 1H, 3-H Ph **4e**,**f**), 7.78 (s, *C(5)H* **4e**), 7.84 (d, *J*=6.10 Hz, *C(5)H* **4f**), 8.29 (d, *J*=9.7 Hz, *C(8)H* **4e**). ^{13}C NMR (DMSO-d_6, 75.47 MHz) δ: 2.5 (CH_3), 12.7 (CH_3), 14.9 (CH_2), 15.0 (CH_2), 15.3 (CH_2), 15.9 (CH_2), 17.4 (CH_3), 20.6 (CH_3), 20.9 (CH_3), 22.3 (CH_3), 57.4 (CH_2), 57.7 (CH_2), 58.4 (CH_2), 59.3 (CH_2), 110.8 (C), 115.6 (CH), 117.9 (CH), 122.2 (CH), 123.6 (CH), 125.9 (C), 126.4 (CH), 128.0 (C), 128.2 (CH), 128.6 (C), 129.1 (CH), 129.2 (C), 129.9 (CH), 131.5 (CH), 132.6 (CH), 134.0 (C), 134.3 (C), 134.5 (C), 139.9 (C), 140.0 (C), 143.7 (C), 188.3 (C). MS m/z 475 (M^+, 21). Anal. Calcd for $C_{24}H_{29}NO_5S_2$: C, 60.61; H, 6.15; N, 2.94. Found: C, 60.78; H, 6.19; N, 2.90.

4.5. Substituted [4,5-di(alkylsulfonyl)-3-furyl]-pyridinium bromides 6a–e (general procedure)

Triethylamine (3 mmol) was added to a stirred solution of pyridinium salt **1** (1 mmol) in EtOH (10 ml), and then a solution of sulfone **3** (1 mmol) was added dropwise. The reaction mixture was heated at 50 °C for 40 min (progress monitored by thin layer chromatography). The solvent was evaporated and the solid residue was dissolved in $CHCl_3$, washed with water, and dried with $MgSO_4$. Then the solution was concentrated and the solid residue was washed with hot acetone and separated by decantation. The solid residue was dissolved in a glacial acetic acid (10 ml), 5–6 fold excess of HBr (48%) and the calculated amount of acetic anhydride for binding water were added. The reaction mixture was heated to 50–60 °C and kept at this temperature for 40–50 min. The crystals of compounds **6a**–**e** were precipitated out with diethyl ether. The acetone solution was evaporated; the solid residue was washed

with warm water (40 °C), and separated by decantation. Final products **4a**–**f** were crystallized and isolated.

4.5.1. 1-[2-(2,4-Dimethylphenyl)-4,5-bis(ethylsulfonyl)-3-furyl]-pyridinium bromide ***6a***. Yield=0.20 g (38%) a white solid with mp 228–229 °C, IR: 1636, 1322, 1148 cm^{-1}. ^1H NMR (DMSO-d_6, 300 MHz) δ: 1.28 (t, 3H, *J* 7.4 Hz, CH_3CH_2), 1.37 (t, 3H, *J* 7.4 Hz, CH_3CH_2), 2.27 (s, 3H, *4-Me* Ph), 2.34 (s, 3H, *2-Me* Ph), 3.71–3.77 (m, 4H, $2CH_2SO_2$), 7.02 (d, 1H, *J* 8.4 Hz, *5-H* Ph), 7.08 (d, 1H, *J* 7.9 Hz, *6-H* Ph), 7.23 (s, 1H, *3-H* Ph), 8.37–8.42 (m, 2H, *3-H*, *5-H* Py), 8.88–8.94 (m, 1H, *4-H* Py), 9.51 (d, 2H, *J* 5.7 Hz, *2-H*, *6-H* Py). ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ: 5.6 (CH_3), 6.8 (CH_3), 19.5 (CH_3), 20.8 (CH_3), 50.5 (CH_2), 51.7 (CH_2), 119.9 (C), 125.1 (C), 126.9 (C), 126.9 (CH), 128.4 (2CH), 129.5 (CH), 132.1 (CH), 138.5 (C), 142.2 (C), 147.4 (C), 147.8 (CH), 149.7 (2CH), 153.4 (C). MS *m*/*z* 434 (M^+–Hal, 14). Anal. Calcd for $C_{21}H_{24}BrNO_5S_2$: C, 49.03; H, 4.70; N, 2.72. Found: C, 48.83; H, 4.64; N, 2.75.

4.5.2. 1-[2-(2,4-Dimethylphenyl)-4,5-bis(propylsulfonyl)-3-furyl]-pyridinium bromide ***6b***. Yield=0.20 g (36%) a white solid with mp 224–225 °C, IR: 1636, 1324, 1148 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ: 0.99 (t, 3H, *J* 7.3 Hz, CH_3CH_2), 1.05 (t, 3H, *J* 7.3 Hz, CH_3CH_2), 1.76–1.92 (m, 2H, CH_3CH_2), 1.95–2.10 (m, 2H, CH_3CH_2), 2.27 (s, 3H, *4-Me* Ph), 2.38 (s, 3H, *2-Me* Ph), 3.61–3.68 (m, 2H, CH_2SO_2), 3.99–4.05 (m, 2H, CH_2SO_2), 6.88 (d, 1H, *J* 7.9 Hz, *5-H* Ph), 7.05 (s, 1H, *3-H* Ph), 7.25 (d, 1H, *J* 8.0 Hz, *6-H* Ph), 8.14–8.20 (m, 2H, *3-H*, *5-H* Py), 8.60–8.66 (m, 1H, *4-H* Py), 9.88–9.90 (m, 2H, *2-H*, *6-H* Py). ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ: 13.0, 13.1, 14.8, 15.8, 20.5, 21.4, 58.4, 59.2, 119.9, 125.1, 127.4, 127.9, 128.2 (2CH), 130.4, 132.4, 139.0, 142.9, 148.1, 148.9, 149.0 (2CH), 154.4. MS *m*/*z* 462 (M^+–Hal, 12). Anal. Calcd for $C_{23}H_{28}BrNO_5S_2$: C, 50.92; H, 5.20; N, 2.58. Found: C, 50.73; H, 5.15; N, 2.56.

4.5.3. 1-[2-(2,4-Dimethylphenyl)-4,5-bis(propylsulfonyl)-3-furyl]-3,5-dimethylpyridinium bromide ***6c***. Yield=0.29 g (50%) a white solid with mp 207–208 °C. IR: 1636, 1322, 1144 cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz) δ: 0.99 (t, 3H, *J* 7.4 Hz, CH_3CH_2), 1.05 (t, 3H, *J* 7.4 Hz, CH_3CH_2), 1.71–1.77 (m, 2H, CH_3CH_2), 1.79–1.85 (m, 2H, CH_3CH_2), 2.29 (s, 3H, *4-Me* Ph), 2.36 (s, 3H, *2-Me* Ph), 2.55 (s, 6H, *3-Me*, *5-Me* Py), 3.72–3.77 (m, 4H, $2CH_2SO_2$), 7.05 (d, 1H, *J* 7.9 Hz, *5-H* Ph), 7.18 (d, 1H, *J* 7.9 Hz, *6-H* Ph), 7.34 (s, 1H, *3-H* Ph), 8.60 (s, 1H, *4-H* Py), 9.35 (s, 2H, *2-H*, *6-H* Py). ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ: 12.4 (CH_3), 12.5 (CH_3), 14.8 (CH_2), 15.7 (CH_2), 17.6 ($2CH_3$), 19.5 (CH_3), 20.8 (CH_3), 57.1 (CH_2), 58.4 (CH_2), 119.9 (C), 124.7 (C), 126.9 (C), 127.1 (CH), 129.6 (CH), 132.2 (CH), 138.3 (2C), 138.5 (C), 142.3 (C), 144.4 (2CH), 147.8 (C), 150.6 (CH), 153.3 (C). MS *m*/*z* 490 (M^+=Hal, 17). Anal. Calcd for $C_{25}H_{32}BrNO_5S_2$: C, 52.62; H, 5.65; N, 2.45. Found: C, 52.41; H, 5.59; N, 2.40.

4.5.3.1. X-ray crystallography. Colorless crystals of compound **6c** were obtained by slow crystallization from ethanol for 3 days at room temperature. Crystal data for **6c**: $C_{25}H_{32}BrNO_5S_2$, M_w=570.55 g mol^{-1}, *T*=153 K, monoclinic, space group *P*2(1)/*c*. Unit cell dimensions: *a*=11.737(4) Å, *b*=17.831(6) Å, *c*=12.957(5) Å, β=96.16(3)°, *V*=2696(2) $Å^3$, *Z*=4, ρ_{calcd}=1.406 g/cm^3, μ=1.71 mm^{-1}. The unit cell parameters and intensities of 4585 reflections were collected on a diffractometer Siemens P3/PC (λMo Kα, graphite monochromator, θ/2θ-scan mode to θ_{max}=25°). The structure was solved by direct method and refined by full-matrix least-squares. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms in the structure were positioned geometrically and were refined as riding atoms. The final *R* factors were R_1=0.072 (2373 independent reflections) and wR_2=0.1225. All calculations were performed using the SHELXL97 programs. Crystallographic data and processing parameters are given in Table 1. The crystallographic coordinates have been deposited to the Cambridge Crystallographic Data Centre, deposition number CCDC-816039. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK or via www.ccdc.cam.ac.uk/conts/retrieving.html.

Table 1
X-ray crystallographic data and processing parameters for **6c**

Empirical formula	$C_{25}H_{32}BrNO_5S_2$
Formula weight	570.55
Wavelength (A)	0.71073
Temperature (K)	153(2)
Crystal system	Monoclinic
Color and shape	Colorless, Prism
Space group	$P2_1/c$
a/Å	11.737(4)
b/Å	17.831(6)
c/Å	12.957(5)
β/°	96.16(3)
Volume ($Å^3$)	2696(2)
Z	4
D_{calcd} (Mg/m^3)	1.406
μ (mm^{-1})	1.714
F(000)	1184
Crystal size/mm	0.30×0.23×0.20
Limiting indices	$0\le h\le 13$, $0\le k\le 21$, $-15\le l\le 15$
θ range (°)	1.75–25.05
Absorption correction	Psi-scan
Psi-scan	0.0961
Data/restraints/parameters	4585/0/307
GOF on (F^2)	1.072
*R*1, *wR*2	0.0720, 0.1255
Largest different peak and hole (e $Å^{-3}$)	1.447 and −1.170

4.5.4. 1-[2-(4-Fluorophenyl)-4,5-bis(propylsulfonyl)-3-furyl]-3,5-dimethylpyridinium bromide ***6d***. Yield=0.07 g (12%) a white solid with mp>230 °C. IR: 1636, 1324, 1144 cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz) δ: 0.96 (t, 3H, *J* 7.42 Hz, CH_3CH_2), 1.05 (t, 3H, *J* 7.42 Hz, CH_3CH_2), 1.68–1.73 (m, 2H, CH_3CH_2), 1.79–1.85 (m, 2H, CH_3CH_2), 2.52 (s, 3H, *3-Me*, Py), 2.55 (s, 3H, *5-Me* Py), 3.65–3.69 (m, 2H, CH_2SO_2), 3.74–3.78 (m, 2H, CH_2SO_2), 7.35–7.39 (m, 4H, *2-H*, *3-H*, *5-H*, *6-H* Ph), 8.73 (s, 1H, 4-H Py), 9.25 (s, 2H, *2-H*, *6-H* Py). ^{13}C NMR (DMSO-d_6, 75.47 Hz) δ: 12.4, 12.5, 14.9, 15.6, 17.8 ($2CH_3$), 57.1, 58.3, 116.9, 117.2, 120.8, 120.9, 122.7, 127.4, 129.4. 129.5, 139.0, 144.3, 147.5, 150.7, 150.9, 162.1, 165.4. MS *m*/*z* 480 (M^+–Hal, 14). Anal. Calcd for $C_{23}H_{27}BrFNO_5S_2$: C, 49.28; H, 4.86; N, 2.50. Found: C, 49.47; H, 4.93; N, 2.58.

4.5.5. 1-[2-(2,4-Dimethylphenyl)-4,5-bis(propylsulfonyl)-3-furyl]-3-methylpyridinium bromide ***6e***. Yield=0.21 g (38%) a white solid with mp 214–215 °C. IR: 1636, 1332, 1140 cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz) δ: 0.99 (t, 3H, *J* 7.6 Hz, CH_3CH_2), 1.08 (t, 3H, *J* 7.6 Hz, CH_3CH_2), 1.70–1.89 (m, 4H, $2CH_3CH_2$), 2.28 (s, 3H, *4-Me* Ph), 2.35 (s, 3H, *2-Me* Ph), 2.55 (s, 3H, *3-Me* Py), 3.68–3.82 (m, 4H, $2CH_2SO_2$), 7.03 (d, 1H, *J* 7.6 Hz, 5-H Ph), 7.15 (d, 1H, *J* 7.6 Hz, *6-H* Ph), 7.23 (s, 1H, *3-H* Ph), 8.29 (t, 1H, *J* 6.9 Hz, *5-H* Py), 8.75 (d, 1H, *J* 8.2 Hz, *4-H* Py), 9.43 (d, 1H, *J* 5.7 Hz, *6-H* Py), 9.55 (s, 1H, *2-H* Py). ^{13}C NMR (DMSO-d_6, 75.47 MHz) δ: 12.3 (CH_3), 12.5 (CH_3), 14.7 (CH_2), 15.6 (CH_2), 17.7 (CH_3), 19.4 (CH_3), 20.8 (CH_3), 57.1 (CH_2), 58.4 (CH_2), 119.9 (C), 124.8 (C), 126.9 (CH), 127.6 (CH), 129.6 (CH), 132.0 (CH), 138.5 (C), 139.1 (C), 142.2 (2C), 145.2 (CH), 146.8 (CH), 147.7 (C), 150.0 (CH), 153.2 (C). MS *m*/*z* 476 (M^+–Hal, 8). Anal. Calcd for $C_{24}H_{30}BrNO_5S_2$: C, 51.79; H, 5.43; N, 2.52. Found: C, 51.95; H, 5.50; N, 2.55.

Supplementary data

Copies of ^1H and ^{13}C NMR spectra of all new compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.03.098. These data include MOL files and InChiKeys of the most important compounds described in this article.

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