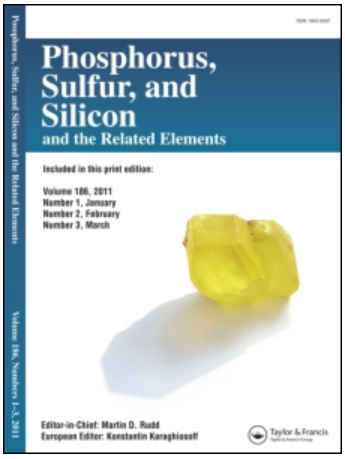

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1,3-Dipolar Cycloaddition of Dipolar Reagents to Bifunctional Bis Olefins in the Presence of Chloramine-T

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1,3-DIPOLAR CYCLOADDITION OF DIPOLAR REAGENTS TO BIFUNCTIONAL BIS OLEFINS IN THE PRESENCE OF CHLORAMINE-T

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The bifunctional bis pyrazolines and bis isoxazolines have been prepared from 1-aroyl-2-styrylsulfonylethenes and 1-arylsulfonyl-2-styrylsulfonylethenes.

Keywords: 1-aroyl-2-styrylsulfonylethenes; 1-arylsulfonyl-2-styrylsulfonylethenes; bis isoxazoles; bis isoxazolines; bis pyrazoles; bis pyrazolines

INTRODUCTION

One of the general methods to accomplish the synthesis of five-membered heterocycles-pyrazolines and isoxazolines is the 1,3-dipolar cycloaddition of ylide to an alkene involving $3+2$ principle.[1] Among the ylides, nitrile imines and nitrile oxides have been used extensively as reactive intermediates in carbon-carbon bond forming reaction processes.[2] They can be generated by the dehydrogenation of araldehyde phenylhydrazones and araldoximes with lead tetraacetate,[3] mercuric acetate,[4] 1-chloro benzotriazole,[5] chloramine-T,[6] among others. However, use of the latter for the in situ generation of dipolar reagents has enthused many organic chemists. In fact we have reported earlier on 1,3-dipolar cycloaddition reaction of chloramine-T catalyzed dipolar reagents with different activated mono olefins.[7]

The successful use of chloramine-T in this front prompted us toward the synthesis of bis pyrazolines and bis isoxazolines by the reaction of bis chalcones and bis sulfones as dipolarophlies with nitrile imines and nitrile oxides as 1,3-dipoles.[8] To continue our interest in this direction,

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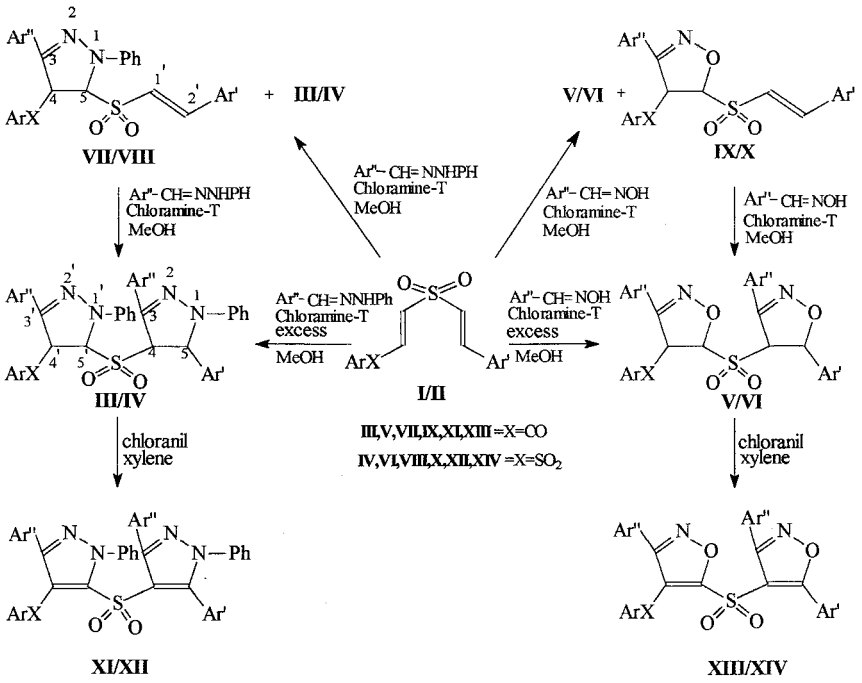
a study on the reaction of bifunctional bis olefinic systems activated by both carbonyl and sulfonyl groups with the latter has been undertaken.

RESULTS AND DISCUSSION

The synthetic scheme involves the reaction of 1-aroyl-2-styrylsulfonylethenes (**I**) and 1-arylsulfonyl-2-styrylsulfonylethenes (**II**) with araldehyde phenylhydrazones/araldoximes in the presence of chloramine-T in MeOH (see Scheme 1). When the reaction was carried out with 1 mmol of **I/II** and 2 mmol of araldehyde phenylhydrazone in the presence of 2 mmol of chloramine-T, a mixture of products were obtained in 3:1 ratio, which were separated through column chromatography (Table I). They were identified as 1-phenyl-3,5-diaryl-2-pyrazolinyl-1′-phenyl-3′-aryl-4′-aroyl/4′-arylsulfonyl-2′-pyrazolinyl-[4,5′]sulfones (**III/IV**, major) and 1-phenyl-3-aryl-4-aroyl/4-arylsulfo-



	Ar	Ar′	Ar″
a	Ph	Ph	Ph
b	4-MePh	Ph	4-OMePh
c	4-ClPh	Ph	4-MePh

SCHEME 1

TABLE I Physical Data of Compounds **III–XIV**

Product	m.p. (°C)	Yield (%) Method A	B	C	Product	m.p. (°C)	Yield (%) Method A
IIIa	184–186	68	75	63	**IXa**	122–123	23
IIIb	176–177	65	76	60	**IXb**	129–130	25
IIIc	169–171	60	71	62	**IXc**	140–141	27
IVa	184–185	62	69	65	**Xa**	136–137	23
IVb	172–174	64	70	61	**Xb**	138–139	24
IVc	169–170	73	67	68	**Xc**	132–133	21
Va	172–173	60	68	64	**XIa**	216–217	67
Vb	164–165	63	67	66	**XIb**	221–223	65
Vc	159–161	59	65	68	**XIc**	204–205	78
VIa	140–141	58	62	62	**XIIa**	218–219	69
VIb	161–163	62	64	60	**XIIb**	207–208	58
VIc	157–159	68	62	58	**XIIc**	214–215	64
VIIa	124–125	20	—	—	**XIIIa**	191–192	69
VIIb	133–134	22	—	—	**XIIIb**	183–184	72
VIIc	131–132	25	—	—	**XIIIc**	187–189	73
VIIIa	118–119	27	—	—	**XIVa**	180–182	70
VIIIb	121–122	24	—	—	**XIVb**	213–214	61
VIIIc	126–127	18	—	—	**XIVc**	211–212	63

[a]Satisfactory elemental analyses were obtained for representative examples of each series C ± 0.24, H ± 0.12, N ± 0.18.

nyl-5-styrylsulfonyl-2-pyrazoline (**VII/VIII**, minor) by their ^{1}H NMR spectra (Table II). Compounds **III/IV** exhibited four doublets at δ 5.78–5.82 (J = 6.1–6.2 Hz), 6.00–6.01 (J = 6.0–6.3 Hz), 6.49–6.52 (J = 6.0–6.2 Hz) and 6.58–6.63 (J = 5.9–6.1) for $C_{4'}$-H, C_4-H, C_5-H and $C_{5'}$-H, respectively. However, compounds **VII/VIII** showed a doublet at δ 6.80–6.84 ($J \approx$ 16.0 Hz), which accounts for $C_{1'}$-H, while $C_{2'}$-H merged with aromatic protons and appeared in the region 6.94–7.91 as a multiplet. Apart from this, two doublets at δ 5.81–5.88 (C_4-H, J = 6.0–6.2 Hz) and 6.58–6.63 (C_5-H, J = 5.9–6.2 Hz) also were observed in their spectrum. A similar reaction of **I/II** with araldoxime also produced a mixture of products (3:1) which were separated by column chromatography. They were found to be 3,5-diaryl-2-isoxazolinyl-3′-aryl-4′-aroyl/4′-arylsulfonyl-2′-isoxazolinyl-[4,5′]sulfones (**V/VI**, major) and 3-aryl-4-aroyl/4-arylsulfonyl-5-styrylsulfonyl-2-isoxazoline (**IX/X**, minor) by their ^{1}H NMR spectra. Compounds **V/VI** exhibited four doublets at δ 5.80–5.86 (J = 6.0–6.3 Hz), 6.10–6.16 (J = 6.0–6.3 Hz), 6.52–6.56 (J = 6.0–6.3 Hz), 6.62–6.65 (J = 6.0–6.3 Hz) which were accounted for $C_{4'}$-H, C_4-H, C_5-H, and $C_{5'}$-H. On the other hand, compounds **IX/X** showed a doublet at 6.84–6.88 ($J \approx$ 16.0 Hz) for $C_{1'}$-H

TABLE II NMR Spectral Data of Compounds **III–XIV**

Compd. no.	^{1}H NMR (δ, ppm)
IIIa	5.81 (d, 1H, $C_{4'}$-H, J = 6.1 Hz), 6.00 (d, 1H, C_4-H, J = 6.3 Hz), 6.54 (d, 1H, C_5-H, J = 6.0 Hz), 6.61 (d, 1H, $C_{5'}$-H, J = 6.1 Hz), 7.18–8.20 (m, 30H, ArH)
IIIb	2.40 (s, 3H, H—CH_3), 3.92 (s, 3H, H—OCH_3), 5.78 (d, 1H, $C_{4'}$-H, J = 6.1 Hz), 6.02 (d, 1H, C_4-H, J = 6.3 Hz), 6.50 (d, 1H, C_5-H, J = 6.1 Hz), 6.63 (d, 1H, $C_{5'}$-H, J = 5.9 Hz), 7.16–8.21 (m, 28H, ArH)
IVa	5.80 (d, 1H, $C_{4'}$-H, J = 6.2 Hz), 6.05 (d, 1H, C_4-H, J = 6.2 Hz), 6.56 (d, 1H, C_5-H, J = 6.0 Hz), 6.63 (d, 1H, $C_{5'}$-H, J = 6.1 Hz), 7.18–8.20 (m, 30H, ArH)
IVb	2.45 (s, 3H, H—CH_3), 3.90 (s, 3H, H—OCH_3), 5.82 (d, 1H, $C_{4'}$-H, J = 6.1 Hz), 6.08 (d, 1H, C_4-H, J = 6.0 Hz), 6.54 (d, 1H, C_5-H, J = 6.2 Hz), 6.61 (d, 1H, $C_{5'}$-H, J = 6.0 Hz), 7.16–8.21 (m, 28H, ArH)
Va	5.86 (d, 1H, $C_{4'}$-H, J = 6.0 Hz), 6.10 (d, 1H, C_4-H, J = 6.2 Hz), 6.57 (d, 1H, C_5-H, J = 6.0 Hz), 6.62 (d, 1H, $C_{5'}$-H, J = 6.1 Hz), 7.18–8.20 (m, 20H, ArH)
Vb	2.42 (s, 3H, H—CH_3), 3.82 (s, 3H, H—OCH_3), 5.84 (d, 1H, $C_{4'}$-H, J = 6.3 Hz), 6.06 (d, 1H, C_4-H, J = 6.0 Hz), 6.56 (d, 1H, C_5-H, J = 6.2 Hz), 6.60 (d, 1H, $C_{5'}$-H, J = 6.1 Hz), 7.20–8.22 (m, 18H, ArH)
VIa	5.88 (d, 1H, $C_{4'}$-H, J = 6.2 Hz), 6.14 (d, 1H, C_4-H, J = 6.2 Hz), 6.59 (d, 1H, C_5-H, J = 6.0 Hz), 6.65 (d, 1H, $C_{5'}$-H, J = 6.1 Hz), 6.99–8.21 (m, 20H, ArH)
VIb	2.35 (s, 3H, H—CH_3), 3.84 (s, 3H, H—OCH_3), 5.79 (d, 1H, $C_{4'}$-H, J = 6.1 Hz), 6.11 (d, 1H, C_4-H, J = 6.3 Hz), 6.56 (d, 1H, C_5-H, J = 6.2 Hz), 6.63 (d, 1H, $C_{5'}$-H, J = 6.2 Hz), 7.03–8.14 (m, 18H, ArH)
VIIa	5.84 (d, 1H, $C_{4'}$-H, J = 6.2 Hz), 6.60 (d, 1H, C_5-H, J = 5.9 Hz), 6.80 (d, 1H, $C_{1'}$-H, J = 16.1 Hz), 6.94–7.79 (m, 21H, ArH and $H_{2'}$)
VIIc	2.33 (s, 3H, H—CH_3), 5.81 (d, 1H, C_4-H, J = 6.0 Hz), 6.63 (d, 1H, C_5-H, J = 6.2 Hz), 6.84 (d, 1H, $C_{1'}$-H, J = 16.2 Hz), 7.04–7.91 (m, 14H, ArH and $H_{2'}$)
VIIIa	5.88 (d, 1H, C_4-H, J = 6.2 Hz), 6.58 (d, 1H, C_5-H, J = 6.1 Hz), 6.82 (d, 1H, $C_{1'}$-H, J = 16.0 Hz), 6.94–7.79 (m, 21H, ArH and $H_{2'}$)
VIIIc	2.38 (s, 3H, H—CH_3), 5.86 (d, 1H, C_4-H, J = 6.1 Hz), 6.62 (d, 1H, C_5-H, J = 6.2 Hz), 6.84 (d, 1H, $C_{1'}$-H, J = 16.2 Hz), 7.04–7.91 (m, 14H, ArH and $H_{2'}$)
IXa	5.82 (d, 1H, C_4-H, J = 6.2 Hz), 6.54 (d, 1H, C_5-H, J = 6.1 Hz), 6.74 (d, 1H, $C_{1'}$-H, J = 16.1 Hz), 6.94–7.79 (m, 16H, ArH and $H_{2'}$)
IXc	2.33 (s, 3H, H—CH_3), 5.94 (d, 1H, C_4-H, J = 6.2 Hz), 6.63 (d, 1H, C_5-H, J = 6.0 Hz), 6.82 (d, 1H, $C_{1'}$-H, J = 16.0 Hz), 7.04–7.91 (m, 14H, ArH and $H_{2'}$)
Xa	5.96 (d, 1H, C_4-H, J = 6.1 Hz), 6.72 (d, 1H, C_5-H, J = 6.2 Hz), 6.88 (d, 1H, $C_{1'}$-H, J = 16.1 Hz), 7.04–7.91 (m, 16H, ArH and $H_{2'}$)
Xc	2.43 (s, 3H, H—CH_3), 5.92 (d, 1H, C_4-H, J = 6.2 Hz), 6.70 (d, 1H, C_5-H, J = 6.2 Hz), 6.85 (d, 1H, $C_{1'}$-H, J = 16.0 Hz), 7.04–7.91 (m, 14H, ArH and $H_{2'}$)

while $C_{2'}$-H merged with aromatic protons and appeared in the region 6.98–7.80 as a multiplet apart from signals due to isoxazoline ring protons (Table II). The olefinic protons in **VII–X** could exist as *cis* and *trans* isomers, but their J values at ~16.0 Hz indicate that they possess

only the *trans* geometry.[9] In **III–VI** there is a possibility of a mixture of diastereomeric bis adducts. However, we could isolate only one pure compound. A small amount of the other isomers, if any, formed could not be isolated. The IR spectra of **III–X** displayed bands in the regions 1133–1156 and 1311–1332 (SO_2), and 1444–1456 (C=N). Apart from these, **III**, **V**, **VII**, and **IX** also exhibited a strong band at 1678–1686 (C=O) and another band around 1630–1644 (C=C) in **VII–X**. However, repetition of these reactions with **I/II** (1 mmol), araldehyde phenylhydrazone/araldoxime (2 mmol) and a two-fold excess of chloramine-T resulted only **III–VI**. On the other hand, when **VII–X** were treated with equimolar proportions of araldehyde phenylhydrazone/araldoxime and chloramine-T furnished once again **III–VI**. The authenticity of **III–VI**, obtained by different routes, was confirmed by their mmp and ^{1}H NMR spectra and their yields in each method were given separately in Table I. The compounds **III–VI** on oxidation with chloranil in xylene[10] gave their respective pyrazoles/isoxazoles **XI–XIV**. The absence of two doublets corresponding to pyrazoline/isoxazoline ring protons in their ^{1}H NMR spectra confirm the formation of **XI–XIV**.

EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are uncorrected. The purity of the compounds was checked by TLC (silica gel H, BDH, ethyl acetate/hexane, 1:3). The IR spectra were recorded on a Perkin-Elmer grating infrared spectrophotometer (ν_{max} in cm^{-1}) model 337 in KBr pellets. The ^{1}H NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on a Varian EM-360 spectrometer (300 MHz) with TMS as an internal standard. The elemental analyses were performed at Dr. Reddy's Research Foundation, Hyderabad, India. The 1-aroyl-2-styrylsulfonylethenes and 1-arylsulfonyl-2-styrylsulfonylethenes were prepared as per the literature procedure.[11]

General Procedure for the Preparation of 1-Phenyl-3,5-diaryl-2-pyrazolinyl-1′-phenyl-3′-aryl-4′-aroyl/4′-arylsulfonyl-2′-pyrazolinyl-[4,5′]sulfones-III/IV/1-phenyl-3-aryl-4-aroyl/4-arylsulfonyl-5-styrylsulfonyl-2-pyrazoline VII/VIII

Method A

To a mixture of **I/II** (10 mmol), araldehyde phenylhydrazone (20 mmol) and chloramine-T (20 mmol) in MeOH (20 ml) was added and refluxed for 8–9 h. Inorganic salts were filtered off. The filtrate was

concentrated and the residue was extracted with methylene chloride (30 ml). The organic extract was washed with water (2 × 25 ml), brine (2 × 25 ml), and dried (an. Na_2SO_4). Evaporation of the solvent under reduced pressure gave a mixture of products, which were separated through a column of silica gel (BDH, 100–200 mesh) using hexane: ethyl acetate (10:1) as the eluent. They were identified as **III/IV** (major) and **VII/VIII** (minor).

General Procedure for the Preparation of 3,5-Diaryl-2-isoxazolinyl-3′-aryl-4′-aroyl/4′-arylsulfonyl-2′-isoxazolinyl-[4,5′]sulfonesV/VI/3-aryl-4-aroyl/4-arylsulfonyl-5-styrylsulfonyl-2-isoxazoline IX/X

Method A

A mixture of **I/II** (10 mmol) in MeOH (20 ml), araldoxime (20 mmol) and chloramine-T (20 mmol) were added and refluxed for 6–7 h. The salts formed, if any were removed by filtration. The filtrate was concentrated and extracted with methylene chloride. The organic extract was washed with water (2 × 25 ml) and brine (2 × 25 ml) and dried (an. Na_2SO_4). The solvent was removed in *vacuo*. The mixtures of products obtained were separated by column chromatography using silica gel (BDH, 100–200 mesh) with hexane: ethyl acetate (10:1) as eluent. The compounds were identified as **V/VI** (major) and **IX/X** (minor).

General Procedure for the Preparation of III–VI

Method B

The compound **I/II** (10 mmol), araldehyde phenylhydrazone (20 mmol)/araldoxime (20 mmol) and a two-fold excess of chloramine-T in MeOH (25 ml) was refluxed for 6–7 h. The salts formed were filtered off. The filtrate was concentrated and the residue was extracted with methylene chloride. The organic extract was washed with water (2 × 25 ml), brine (2 × 25 ml), and dried (an. Na_2SO_4). Evaporation of the solvent under reduced pressure gave crude product, which was purified through a column of silica gel (BDH, 100–200 mesh) using hexane: ethyl acetate (10:1) as the eluent to provide pure **III–VI**.

Method C

An equimolar (10 mmol) mixture of **VII/VIII/IX/X**, araldehyde phenylhydrazone/araldoxime and chloramine-T in MeOH (20 ml) was refluxed for 5–6 h. The reaction mixture was processed as mentioned previously to provide pure **III–VI**.

Dehydrogenation of III–VI

A mixture of **III/IV/V/VI** (10 mmol) and chloranil (11 mmol) in xylene (20 ml) was refluxed for 30–32 h and the organic layer was separated and washed with 1N NaOH, water and dried (an. Na_2SO_4). The solvent was removed under reduced pressure. The solid obtained was purified by recrystallization from MeOH to provide **XI–XIV** respectively.

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