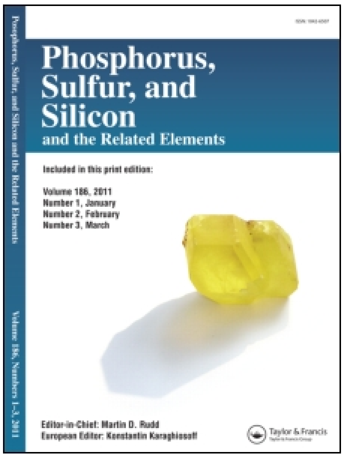

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SYNTHESIS AND SPECTRAL STUDIES OF SOME NEW [(ALKOXYCARBONYLVINYL)ARYL- AND BENZYLSULFONYLMETHYL] SULFONES

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SYNTHESIS AND SPECTRAL STUDIES OF SOME NEW [(ALKOXYCARBONYLVINYL)ARYL- AND BENZYLSULFONYLMETHYL] SULFONES

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Some new 1,1,2-trisubstituted ethylenic sulfones have been prepared by the condensation of aryl- and benzylsulfonylmethylsulfonylacetic acid esters with araldehydes.

Key words: 1,1,2-Trisubstituted ethylenic sulfones; Knoevenagel condensation; aryl- and benzylsulfonylmethylsulfonylacetic acid esters.

INTRODUCTION

A number of 1,2-disubstituted ethylenic sulfones were prepared by the condensation of alkyl or aryl sulfonylacetic acids with araldehydes in the presence of ammonia in glacial acetic acid.[1,2] Adopting the same method several workers have obtained them in fairly good yields in the presence of cyclohexylamine,[3] ammonium acetate[4] or benzylamine[5] as catalysts instead of ammonia. However, the esters of sulfonylacetic acid have not been well exploited as synthons for a similar purpose.[6–9]

A number of unsaturated sulfones were found to be useful as synthons for the synthesis of varied carbocyclic[10] and heterocyclic[11,12] systems. The sulfones have also gained importance as fungicides, algicides and medicinal agents.[13] Some of the sulfonyl esters gave promising results as anticancer agents.[14] These observations and our continued interest in this field[15] prompted us to report the synthesis of some 1,1,2-trisubstituted α, β-ethylenic sulfonyl esters.

RESULTS AND DISCUSSION

The [(alkoxycarbonylvinyl)aryl- and benzylsulfonylmethyl] sulfones (**IV**) have been obtained by the condensation of aryl- and benzylsulfonylmethylsulfonylacetic acid

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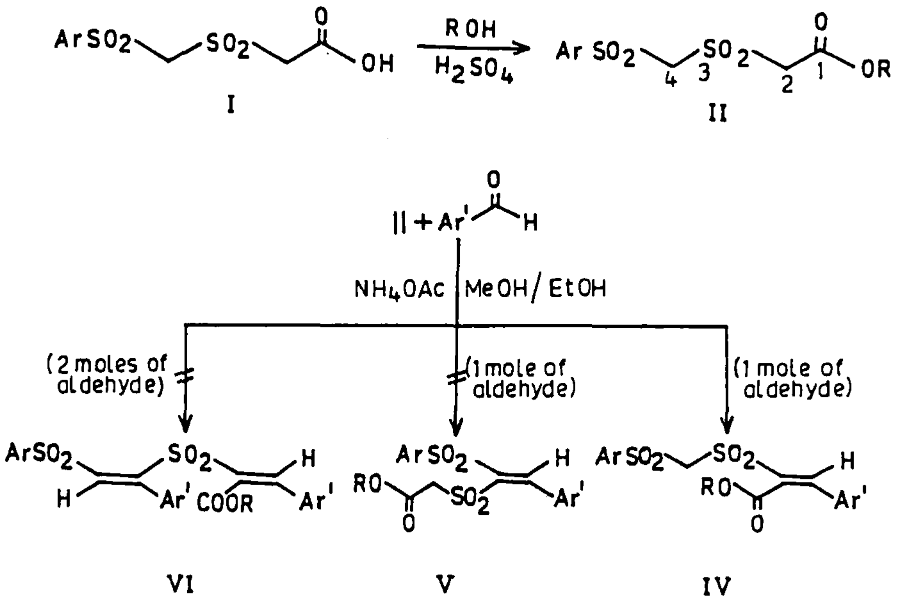
methyl/ethyl esters (II) with araldehydes (III) in the presence of a catalytic amount of ammonium acetate in methanol/ethanol (Scheme and Table I). Monitoring of the crude reaction mixture by TLC does not indicate the presence of the isomeric co-product V. When the reaction was carried out with two moles of aldehyde and on accelerating the reaction conditions the product VI could not be obtained. Obviously, the generation of carbanion under the conditions of the reaction is rather difficult from the methylene group at C-4. It may be considered that the facile formation of the carbanion from the methylene group at C-2 should have rendered possible the condensation of aldehyde to give the product IV only.

The IR spectral data of compounds IV (Table II) revealed that substituents in the aromatic ring $=CHAr^1$ do not have any significant effect on the frequency of



IV	a	Ar = C_6H_5	Ar'=C_6H_5	R=CH_3
	b	Ar = C_6H_5	Ar'=4-$CH_3C_6H_4$	R=CH_3
	c	Ar = 4-ClC_6H_4	Ar'=4-ClC_6H_4	R=CH_3
	d	Ar = 4-ClC_6H_4	Ar'=4-$CH(CH_3)_2C_6H_4$	R=CH_3
	e	Ar = 4-ClC_6H_4	Ar'=4-ClC_6H_4	R=C_2H_5
	f	Ar = 4-ClC_6H_4	Ar'=4-$CH(CH_3)_2C_6H_4$	R=C_2H_5
	g	Ar = 4-ClC_6H_4	Ar'=2-$C_{10}H_7$	R=C_2H_5
	h	Ar = $C_6H_5CH_2$	Ar'=4-ClC_6H_4	R=CH_3
	i	Ar = $C_6H_5CH_2$	Ar'=3,4-$Cl_2C_6H_3$	R=CH_3
	j	Ar = $C_6H_5CH_2$	Ar'=2-$C_{10}H_7$	R=CH_3
	k	Ar = 4-$ClC_6H_4CH_2$	Ar'=4-ClC_6H_4	R=CH_3
	l	Ar = 4-$ClC_6H_4CH_2$	Ar'=4-$CH(CH_3)_2C_6H_4$	R=CH_3
	m	Ar = 4-$ClC_6H_4CH_2$	Ar'=4-$CH(CH_3)_2C_6H_4$	R=C_2H_5
	n	Ar = 4-$ClC_6H_4CH_2$	Ar'=3,4-$Cl_2C_6H_3$	R=C_2H_5

SCHEME

TABLE I

Physical data of [(methoxy/ethoxycarbonylvinyl)aryl- and benzylsulfonylmethyl] sulfones (IV)

Compd. No.	Yield (%)	m. p. (°C)	Molecular formula	m. wt.	Found(%) (Calc.)	
					C	H
IV a	70	158-159^a	$C_{17}H_{16}O_6S_2$	380	53.45 (53.68)	4.12 (4.21)
b	72	163-164^a	$C_{18}H_{18}O_6S_2$	394	54.52 (54.81)	4.68 (4.60)
c	78	205-206^a	$C_{17}H_{14}Cl_2O_6S_2$	449	45.65 (45.44)	3.22 (3.14)
d	68	124-125^a	$C_{20}H_{21}ClO_6S_2$	457	52.35 (52.57)	4.56 (4.63)
e	75	198-199^a	$C_{18}H_{16}Cl_2O_6S_2$	463	46.84 (46.66)	3.59 (3.48)
f	65	168-169^a	$C_{21}H_{23}ClO_6S_2$	471	53.78 (53.55)	5.05 (4.92)
g	62	192-193^b	$C_{22}H_{19}ClO_6S_2$	479	54.85 (55.17)	3.90 (4.00)
h	80	155-156^a	$C_{18}H_{17}ClO_6S_2$	429	50.18 (50.40)	4.12 (4.00)
i	75	169-170^b	$C_{18}H_{16}Cl_2O_6S_2$	463	46.86 (46.66)	3.39 (3.48)
j	60	170-171^b	$C_{22}H_{20}O_6S_2$	445	59.20 (59.44)	4.45 (4.54)
k	76	191-192^c	$C_{18}H_{16}Cl_2O_6S_2$	463	46.84 (46.66)	3.40 (3.48)
l	70	164-165^a	$C_{21}H_{23}ClO_6S_2$	471	53.32 (53.55)	5.05 4.92)
m	68	159-160^a	$C_{22}H_{25}ClO_6S_2$	485	54.70 (54.48)	5.32 (5.20)
n	78	153-154^b	$C_{19}H_{17}Cl_3O_6S_2$	512	44.75 (44.58)	3.43 (3.35)

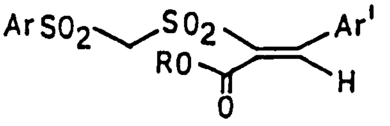
Solvent for crystallization: a) EtOAc b) C_6H_6+EtOAc c) n-Pr OH

TABLE II

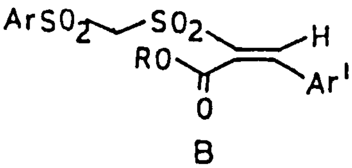
IR and ¹H NMR spectral data of [(methoxy/ethoxycarbonylvinyl)aryl- and benzylsulfonylmethyl] sulfones (IV)

Compd. No.	IR KBr (ν cm^{-1})			^{1}H NMR (δ, ppm)			
	C=O	SO_2		C=CH-	$SO_2CH_2SO_2$	$ArCH_2$	C=CH-	Aromatic protons
IV a	1740	1335	1125	830	4.60	-	8.00	7.10 - 7.85
b	1735	1330	1130	815	4.65	-	8.05	7.05 - 7.75
c	1745	1335	1120	825	4.70	-	8.15	7.10 - 7.95
d	1730	1325	1130	820	4.60	-	8.10	7.15 - 7.90
e	1745	1340	1125	840	4.65	-	8.25	7.20 - 7.85
f	1740	1330	1145	835	4.80	-	8.15	7.10 - 7.80
g	1735	1335	1115	810	4.85	-	8.10	7.15 - 7.75
h	1740	1340	1120	815	4.70	4.85	8.05	7.10 - 7.85
i	1745	1345	1135	830	4.60	4.95	8.10	7.05 - 7.90
j	1740	1335	1130	825	4.75	4.80	8.05	7.10 - 7.95
k	1745	1330	1120	840	4.65	4.80	8.20	7.20 - 8.00
l	1740	1325	1145	830	4.65	4.85	8.25	7.15 - 7.95
m	1745	1340	1135	825	4.80	4.90	8.15	7.20 - 7.90
n	1750	1345	1130	835	4.75	4.95	8.20	7.10 - 7.95

the C=O stretching vibration of the ester group. If the carbonyl group is situated *trans* to the aryl moiety as shown in structure **A** there would be conjugative interaction of the carbonyl and aryl groups through >C=CH and the substituent in the aryl moiety will increase or decrease the carbonyl stretching frequency depending upon its nature.[16] Perusal of the data in Table II indicates that there is no such conjugative interaction. It may be presumed that steric factors would permit the aryl moiety to be in *cis* position to the alkoxycarbonyl group as in structure **B**.



A



B

The ^{1}H NMR spectra of the compounds **IV** exhibited δ_H values at 4.60–4.85 ppm for the methylene protons. In fact, the methylene protons, ArCO$\underline{CH_2}$ showed the chemical shift values at 4.75 ppm in $ArCOCH_2SO_2CH_2CO_2H$ and $ArCOCH_2SO_2CH{=}CH\text{-}Ar^1$, while they appeared at 4.45 ppm when adjacent to the carboxylic group.[17] This supports to the formation of the compounds **IV** only.

EXPERIMENTAL

All melting points were determined on a Mel-Temp apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer 577 infrared spectrometer as KBr pellets. The ^{1}H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R-32 spectrometer in $CDCl_3$. The chemical shifts were measured in ppm relative to TMS as an internal standard. The elemental analyses were performed by Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, India.

Methyl/ethyl esters of aryl- and benzylsulfonylmethylsulfonylacetic acid (**II**) were obtained by the esterification of the corresponding acids[18] with methanol/ethanol in sulphuric acid and were purified by recrystallization from methanol: phenylsulfonylmethylsulfonylacetic acid methyl ester, m. p. 84–85°C; 4-chlorophenylsulfonylmethylsulfonylacetic acid methyl ester, m. p. 114–115°C; 4-chlorophenylsulfonylmethylsulfonylacetic acid ethyl ester, m. p. 70–72°C; benzylsulfonylmethylsulfonylacetic acid methyl ester, m. p. 90–91°C; 4-chlorobenzylsulfonylmethylsulfonylacetic acid methyl ester, m. p. 101–103°C; 4-chlorobenzylsulfonylmethylsulfonylacetic acid ethyl ester, m. p. 98–99°C.

*Condensation of aryl- and benzylsulfonylmethylsulfonylacetic acid esters (**II**) with araldehydes (**III**) General Procedure:* A solution of 10 mmol of **II** in 15 ml methanol/ethanol was treated with 10 mmol of **III** in the presence of 0.5 g of ammonium acetate. The reaction mixture was refluxed for 30–45 min. The contents were cooled and any product that separated was removed by filtration. The reaction mixture or the filtrate was refrigerated overnight. The resulting solid was collected on a Buchner funnel. The combined solid thus obtained was recrystallized from appropriate solvent to give pure **IV**. The purity was tested by TLC (silica gel-H, BDH; ethyl acetate/hexane 2:3).

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