A Novel Phase – Transfer Catalysed Cycloaddition of Carbonyl-Stabilized Sulfur Ylides to Vinylic Sulfones

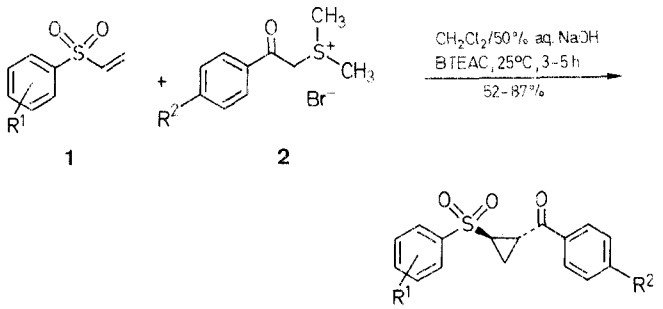
D. Bhaskar Reddy,* P.S. Reddy, B.V. Reddy, P.A. Reddy

Department of Chemistry, Sri Venkateswara University Tirupati 517 502, India.

In our current studies on the chemistry and synthetic utility of carbonyl stabilized sulfur ylides, we have found that the cycloaddition of dimethylsulfonium phenacylides to aryl vinyl sulfones to be a useful general approach to 1-arylsulfonyl-2-aroylcyclopropanes **3**.

Although phase-transfer conditions have been exploited for very many reactions,[1] their application to cyclopropanation reactions of sulfonyl activated double bonds is not well explored. Stabilized sulfur ylides and the more reactive non-stabilized ylides have both been utilized for cyclopropanations,[2-5] whereby rigorous reaction conditions have often been employed which often result in poor yields. The reaction of vinylic sulfones with carbonyl stabilized sulfur ylides, whether in a two-phase system or not, has not to our knowledge been reported, even though a few instances of the cycloaddition of sulfur ylides to chalcones under phase-transfer conditions are known.[6,7]

Hence, we now wish to report the application of phase-transfer catalysis to the synthesis of a variety of 1-arylsulfonyl-2-aroylcyclopropanes **3** by the cycloaddition reaction of aryl vinyl sulfones **1** with dimethylphenacyl sulfonium bromides **(2)** in dichloromethane with 50% aqueous sodium hydroxide in the presence of benzyltriethyl ammonium chloride (BTEAC) (Table).



BTEAC = benzyltriethylammonium chloride

Cyclopropanation to the activated double bonds was done earlier by generating the ylide[8] *in situ* from the salt or by preparing the stable ylide first.[4] Both procedures, however, require perfectly anhydrous conditions and are time consuming. These difficulties have been overcome by adopting phase-transfer conditions, which avoids the obvious problem of

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Table. 1-Arylsulfonyl-2-aroylcyclopropanes **3** Prepared.

Product 3	R^1	R^2	Yield (%)	m.p.[a] (°C)	Molecular Formula[b]	IR (KBR) (cm^{-1})[c] Ring deformation mode	ν_{SO_2}	$\nu_{C=O}$	^{1}H-NMR ($CDCl_3$/TMS)[d] δ (ppm)
a	H	H	52	153–154	$C_{16}H_{14}O_3S$ (286.3)	1025	1320, 1140	1675	2.30–2.66 (m, 2H, CH_2); 3.40–3.80 (m, 2H, CH)[2]; 7.30–7.86 (m, 10H_{arom}).
b	H	Cl	63	164–165	$C_{16}H_{13}ClO_3S$ (320.8)	1020	1320, 1155	1675	2.46–2.88 (m, 2H, CH_2); 3.52–3.84 (m, 2H, CH); 7.34–8.0 (m, 9H_{arom}).
c	H	Br	69	198–200	$C_{16}H_{12}BrO_3S$ (364.2)	1010	1305, 1165	1665	–
d	4-Cl	Cl	87	167–168	$C_{16}H_{12}Cl_2O_3S$ (355.2)	1025	1305, 1140	1670	2.38–2.80 (m, 2H, CH_2); 3.36–3.76 (m, 2H, CH); 7.42–8.04 (m, 8H_{arom}).
e	4-Cl	Br	79	203–205	$C_{16}H_{12}BrClO_3S$ (399.7)	1020	1315, 1170	1670	2.40–2.76 (m, 2H, CH_2); 3.50–3.86 (m, 2H, CH); 7.40–8.10 (m, 8H_{arom}).
f	4-Br	Cl	82	155–156	$C_{16}H_{12}BrClO_3S$ (399.7)	1015	1310, 1140	1675	2.56–2.90 (m, 2H, CH_2); 3.36–3.80 (m, 2H, CH); 7.46–8.15 (m, 8H_{arom});
g	4-Br	CH_3	64	140–142	$C_{17}H_{15}BrO_3S$ (379.3)	1015	1315, 1135	1660	2.38 (s, 3H, CH_3); 2.46–2.72 (m, 2H, CH_2); 3.38–3.74 (m, 2H, CH); 7.38–7.96 (m, 8H_{arom}).
h	4-CH_3	Cl	57	183–184	$C_{17}H_{15}ClO_3S$ (334.8)	1025	1315, 1135	1680	2.38 (s, 3H, CH_3); 2.42–2.82 (m, 2H, CH_2); 3.44–3.82 (m, 2H, CH); 7.46–8.14 (m, 8H_{arom}).
i	3,4-Cl_2	H	74	211–212	$C_{16}H_{12}Cl_2O_3S$ (355.2)	1020	1310, 1160	1655	–
j	3,4-Cl_2	Br	79	191–192	$C_{16}H_{11}BrCl_2O_3S$ (434.1)	1020	1315, 1170	1675	2.32–2.68 (m, 2H, CH_2); 3.40–3.76 (m, 2H, CH); 7.40–8.10 (m, 7H_{arom}).
k	3,4-Cl_2	CH_3	60	145–146	$C_{17}H_{14}Cl_2O_3S$ (369.2)	1025	1310, 1145	1665	–

[a] Melting points are uncorrected.
[b] Satisfactory microanalyses obtained: C ± 0.22, H ± 0.15.
[c] Recorded on a Beckman Model 18-A spectrophotometer.
[d] 80 MHz spectra recorded on a Brucker Spectrospin spectrometer.

generation and preservation of the dimethylsulfonium phenacylides. Thus, the advantages achieved by the present method are higher yields, shorter reaction times and milder reaction conditions.

The IR spectra (2 max in cm^{-1}) of compounds **3** display medium to strong intensity bands in the region 1040–1010, characteristic of the cyclopropane deformation mode of the ring[3] (Table). They also exhibited strong bands in the regions 1320–1305 and 1170–1135 (ν SO_2)[3] and 1680–1655 cm^{-1} (ν C=O).[4]

The ^{1}H-NMR spectra of the compounds in the present investigation exhibited complex multiplets for the cyclopropyl methylene and methine protons. The deshielding effect of the sulfonyl and the carbonyl group is almost the same at the carbon atoms to which they are attached. Hence, the two methine protons can be considered as chemically equivalent and magnetically non-equivalent. Thus the four protons (methylene and methine) of the 1,2-disubstituted cyclopropane shows an AA′ BB′ pattern, which may be regarded as typical for the *trans* configuration.[9]

All the cyclopropyl keto sulfones **(3)** obtained are new products. The procedure herein described constitutes an elegant and simple method for obtaining 1-arylsulfonyl-2-aroylcyclopropanes under mild reaction conditions.

1-Arylsulfonyl-2-aroylcyclopropanes 3; General Procedure:
A mixture of aryl vinyl sulfone[10] (10 mmol), dimethylphenacylsulfonium bromide[11] (11 mmol), dichloromethane (6 ml) and 50% aqueous sodium hydroxide (4 ml) are placed in a flask equipped with a magnetic stirrer. The contents of the flask are stirred for 20 to 30 min. Benzyltriethylammonium chloride (500 mg) is added and stirring is continued for 3–5 h at room temperature. The reaction mixture is diluted with water (50 ml). The organic layer is separated, washed with water, brine and dried over sodium sulfate. Evaporation of solvent under reduced pressure yields a crude solid, which is filtered through a column of silica gel (60–120 mesh, BDH, with hexane/ether, 3:2, as eluent) to give **3** as a crystalline solid, the purity of which is checked by TLC (Table).

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