Double Michael Addition Reactions to Tetrakis Sulfonyl Activated Olefins

Venkatapuram Padmavathi,* Dandu Rangayapalle Chinna Venkata Subbaiah and Boggu Jagan Mohan Reddy

> Department of Chemistry, Sri Venkateswara University, Tirupati 517 502, India Received August 30, 2004

A new class of bis Michael adducts are prepared from 1,3-bis-[2-(2-arylethenesulfonyl)-vinyl]-benzenes and 1,4-bis-[2-(2-arylethenesulfonyl)-vinyl]-benzenes by double Michael addition reaction with active methylene compounds.

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The carbon-carbon bond forming reactions are important in achieving the desired molecular architecture. In fact, the development of efficient and expedient methodologies for the synthesis of activated alkenes remains a worthwhile task, which would serve as building blocks for various carbocyclic and heterocyclic systems. Thus the improvement and design of a new reaction system is a fundamental approach for any synthetic organic chemist. Over the years, our research group has been actively involved in this area. In recent past we have reported an unusually simple approach for the synthesis of E, Z-bis (styryl) sulfones [1-2] and mono and bis unsaturated oxosulfones and bis sulfones [3-4]. In continuation of our interest in activated olefins, herein we report a new class of unsaturated sulfones, 1,3- and 1,4-bis-[(arylethenesulfonyl)-vinyl]-benzenes 1 and 2 which have been used as Michael acceptors in double Michael addition.

The Knoevenagel reaction of 2-arylethenesulfonylacetic acid [1] with 1,3- and 1,4-benzenedicarboxaldehyde in the

presence of benzylamine in acetic acid resulted in 1,3- and 1,4-bis-[(arylethenesulfonyl)-vinyl]-benzenes 1 and 2. The IR spectra of 1 and 2 showed absorption bands in the regions 1305-1315, 1135-1150 (SO₂) and 1620-1635 cm⁻¹ (C=C). The presence of doublets at δ 7.75-7.81 (H_D), 7.54- $7.58 (H_A)$, $7.01-7.06 (H_C)$ and $6.60-6.64 (H_B)$ with coupling constants: $J_{AB} = 10.5\text{-}10.8$, $J_{CD} = 15.3\text{-}15.8$ Hz in their ¹H NMR spectra indicated that H_A, H_B and H_C, H_D are cis and trans oriented, respectively. These compounds have been utilized as Michael acceptors in double Michael addition reaction with different nucleophiles viz., dimethyl malonate, ethyl cyanoacetate and malononitrile. In recent past we have been actively engaged in the double Michael addition of active methylene compounds to bis unsaturated systems [5-8]. When the reaction has been carried out in the presence of piperidine [9], sulfinic acid [10], phosphorus trichloride [11] afforded open chain adducts while cyclic products have been obtained in the presence of sodium methoxide or sodium hydroxide [12]. These cyclic

adducts have been used to prepare a variety of spiro heterocycles [13-15]. In continuation of our ongoing program to develop some more interesting heterocycles, we thought of extending the double Michael addition to newly prepared tetrakis unsaturated sulfones.

The reaction of 1,3- and 1,4-bis-[(arylethenesulfonyl)-vinyl]-benzenes **1** and **2** with active methylene compounds such as dimethyl malonate, ethyl cyanoacetate and malononitrile in the presence of Triton-B in THF resulted in the formation of dimethyl 3,3'-1,3- and 1,4-phenylene bisthiopyrandicarboxylate dioxides **3** and **4**, ethyl 3,3'-1,3- and 1,4-phenylene bis-cyanothiopyrancarboxylate dioxides **5** and **6**, 3,3'-1,3- and 1,4-phenylene bisthiopyrandicarbonitrile dioxides **7** and **8** (Scheme). In compounds **3**-**8** there are stereo centers and as a result a mixture of diastereomeric bis-adducts could be formed. However we could isolate only one pure compound when the reaction mixture was passed through a column of silica gel. A small

amount of the other isomers, if any, formed could not be isolated by this process. The IR spectra of compounds 3-8 displayed absorption bands in the region 1305-1315 and 1135-1150 cm⁻¹ (SO₂). The compounds **3-6** showed bands at 1710-1730 cm⁻¹ (CO₂R). Apart from this, compounds 5-8 exhibited bands in the region 2240-2250 cm⁻¹ (CN). The methine and methylene protons of these compounds (3-8) in ¹H NMR spectra showed three doublet of doublets thus exhibiting an AMX splitting pattern. The doublet of doublets observed at δ 4.28-4.34, 3.92-3.97 and 2.91-2.96 are assigned to H_A , H_M and H_X , respectively. The J values indicated that HA, HM are trans and HA, HX are cis oriented while H_M, H_X are *geminal*. Apart from this 3 and 4 displayed two sharp signals in the regions δ 3.54-3.57 and 3.62-3.67 due to equatorial and axial carbomethoxy groups. The downfield absorption may be assigned to axial carbomethoxy group while the upfield shift to an equatorial one [5,7,16]. The ¹³C NMR spectra of **3-8** showed sig-

Table 1

Physical data of compounds dimethyl 3,3'-1,3- and 1,4-phenylene bis-thiopyran-dicarboxylate dioxides 3 and 4, ethyl 3,3'-1,3- and 1,4-phenylene bis-cyanothiopyran-carboxylate dioxides 5 and 6, 3,3'-1,3- and 1,4-phenylene bis-thiopyran-dicarbonitrile dioxides 7 and 8.

Compd.	Ar	m.p.	Yield	Mol. Formula	Calcd. (Found) %		
No.		(°C)	(%)	(Mol. Wt)	C	Н	N
3a	Ph	158-160	68	C ₃₆ H ₃₈ O ₁₂ S ₂	59.49	5.27	
				(726.81)	(59.52)	(5.30)	
3b	4-Me.Ph	163-165	73	$C_{38}H_{42}O_{12}S_2$	60.46	5.61	
				(754.86)	(60.36)	(5.65)	
3c	4-Cl.Ph	202-204	77	$C_{36}H_{36}Cl_2O_{12}S_2$	54.34	4.56	
				(795.70)	(54.40)	(4.54)	
4a	Ph	169-171	71	$C_{36}H_{38}O_{12}S_2$	59.49	5.27	
				(726.81)	(59.41)	(5.22)	
4b	4-Me.Ph	201-203	65	$C_{38}H_{42}O_{12}S_2$	60.46	5.61	
				(754.86)	(60.53)	(5.64)	
4c	4-Cl.Ph	222-224	76	$C_{36}H_{36}Cl_2O_{12}S_2$	54.34	4.56	
				(795.70)	(54.46)	(4.52)	
5a	Ph	153-155	66	$C_{36}H_{36}N_2O_8S_2$	62.77	5.27	4.07
				(688.81)	(62.83)	(5.29)	(4.00)
5b	4-Me.Ph	168-170	69	$C_{38}H_{40}N_2O_8S_2$	63.67	5.62	3.91
_				(716.86)	(63.61)	(5.67)	(3.99)
5c	4-Cl.Ph	196-198	73	$C_{36}H_{34}Cl_2N_2O_8S_2$	57.07	4.52	3.70
_				(757.70)	(57.16)	(4.47)	(3.81)
6a	Ph	161-163	71	$C_{36}H_{36}N_2O_8S_2$	62.77	5.27	4.07
-				(688.81)	(62.84)	(5.23)	(4.12)
6b	4-Me.Ph	203-205	76	$C_{38}H_{40}N_2O_8S_2$	63.67	5.62	3.91
_	4 61 70	240.220	5 0	(716.86)	(63.54)	(5.54)	(3.98)
6c	4-Cl.Ph	218-220	78	$C_{36}H_{34}Cl_2N_2O_8S_2$	57.07	4.52	3.70
_	P.1	4 - 5 - 4 - 5		(757.70)	(57.13)	(4.50)	(3.78)
7a	Ph	165-167	63	$C_{32}H_{26}N_4O_4S_2$	64.63	4.41	9.42
_,	436.79	150 151		(594.71)	(64.55)	(4.45)	(9.39)
7 b	4-Me.Ph	172-174	68	$C_{34}H_{30}N_4O_4S_2$	65.57	4.86	9.00
_	4 CL DI	200 211	<i>c</i> 4	(622.76)	(65.62)	(4.92)	(9.09)
7c	4-Cl.Ph	209-211	64	$C_{32}H_{24}Cl_2N_4O_4S_2$	57.92	3.65	8.44
0	DI	160 171	70	(663.59)	(57.85)	(3.58)	(8.53)
8a	Ph	169-171	70	$C_{32}H_{26}N_4O_4S_2$	64.63	4.41	9.42
OL.	4 M - Dl-	205 207	<i>(</i> 0	(594.71)	(64.57)	(4.34)	(9.37)
8b	4-Me.Ph	205-207	69	$C_{34}H_{30}N_4O_4S_2$	65.57	4.86	9.00
0.	4 Cl Db	221 222	72	(622.76)	(65.65)	(4.94)	(8.94)
8c	4-Cl.Ph	231-233	72	$C_{32}H_{24}Cl_2N_4O_4S_2$	57.92	3.65	8.44
				(663.59)	(57.99)	(3.58)	(8.50)

Table 2 Spectroscopic Data of Compounds 1-8

Compd. No	1 H NMR δ , ppm	13 C NMR δ , ppm
1a	6.64 (d, 2H, H_B , J =10.6 Hz), 7.03 (d, 2H, H_C , J =15.5 Hz), 7.14-7.30 (m, 14H, Ar-H), 7.57 (d, 2H, H_A , J =10.6 Hz), 7.78 (2H, H_D , J =15.5 Hz)	125.6 (CH-SO ₂), 145.7 (CH-Ar)
1b	2.36 (s, 6H, CH ₃), 6.61 (d, 2H, H _B , J =10.8 Hz), 7.02 (d, 2H, H _C , J =15.6 Hz), 7.04-7.34 (m, 12H, Ar-H), 7.56 (d, 2H, H _A , J =10.8 Hz), 7.79 (2H, H _D , J =15.6 Hz)	124.8 (CH-SO ₂), 143.7 (CH-Ar)
1c	6.63 (d, 2H, H _B , <i>J</i> =10.5 Hz), 7.05 (d, 2H, H _C , <i>J</i> =15.4 Hz), 7.16-7.34 (m, 12H, Ar-H), 7.56 (2H, H _A , <i>J</i> =10.5 Hz), 7.81 (d, 2H, H _D , <i>J</i> =15.4 Hz)	126.7 (CH-SO ₂), 142.8 (CH-Ar)
2a	6.63 (d, 2H, H _B , <i>J</i> =10.8 Hz), 7.01 (d, 2H, H _C , <i>J</i> =15.8 Hz), 7.16-7.33 (m, 14H, Ar-H), 7.56 (2H, H _A , <i>J</i> =10.8 Hz), 7.80 (d, 2H, H _D , <i>J</i> =15.6 Hz)	124.6 (CH-SO ₂), 144.7 (CH-Ar)
2b	2.34 (s, 6H, CH ₃), 6.64 (d, 2H, H _B , <i>J</i> =10.6 Hz), 7.01-7.25 (m, 12H, Ar-H), 7.06 (d, 2H, H _C , <i>J</i> =15.3 Hz), 7.58 (2H, H _A , <i>J</i> =10.6 Hz),	125.9 (CH-SO ₂), 145.3 (CH-Ar)
2c	7.75 (d, 2H, H _D , <i>J</i> =15.3 Hz) 6.60 (d, 2H, H _B , <i>J</i> =10.7 Hz), 7.04 (d, 2H, H _C , <i>J</i> =15.4 Hz), 7.20-7.28 (m, 12H, Ar-H), 7.54 (d, 2H, H _A , <i>J</i> =10.7 Hz), 7.79 (2H, H _D , <i>J</i> =15.4 Hz)	126.6 (CH-SO ₂), 144.3 (CH-Ar)
3a	2.94 (dd, 4H, H_X , J_{AX} = 5.3, J_{MX} = 15.7 Hz), 3.56 (s, 6H, eq-OCH ₃), 3.67 (s, 6H, ax-OCH ₃), 3.93 (dd, 4H, H_M , J_{AM} = 10.5 Hz), 4.31 (dd,	27.9 (C-3) 28.2 (C-5), 50.7 & 52.8 (OCH ₃), 56.0 (C-2 & C-6), 68.0 (C-4), 176.0 (C=O)
3b	4H, H_A), 6.95-7.18 (m, 14H, Ar-H) 2.36 (s, 6H, CH ₃), 2.91 (dd, 4H, H_X , J_{AX} = 5.2, J_{MX} = 15.9 Hz), 3.54 (s, 6H, eq-OCH ₃), 3.63 (s, 6H, ax-OCH ₃), 3.94 (dd, 4H, H_M , J_{AM} =	20.9 (CH ₃), 28.5 (C-3) 28.8 (C-5), 50.2 & 52.3 (OCH ₃), 56.4 (C-2 & C-6), 67.2 (C-4), 174.8 (C=O)
3c	10.7 Hz), 4.33 (dd, 4H, H _A), 6.95-7.12 (m, 12H, Ar-H) 2.91 (dd, 4H, H _X , J_{AX} = 5.5, J_{MX} = 15.7 Hz), 3.57 (s, 6H, eq-OCH ₃), 3.62 (s, 6H, ax-OCH ₃), 3.96 (dd, 4H, H _M , J_{AM} = 10.4 Hz), 4.29 (dd,	28.4 (C-3) 29.6 (C-5), 50.5 & 53.2 (OCH ₃), 56.3 (C-2 & C-6), 68.6 (C-4), 176.2 (C=O)
4a	4H, H _A), 6.96-7.18 (m, 12H, Ar-H) 2.95 (dd, 4H, H _X , J _{AX} = 5.2, J _{MX} = 15.8 Hz), 3.57 (s, 6H, eq-OCH ₃),	28.3 (C-3 & C-5), 49.9 & 51.7 (OCH ₃), 56.4 (C-2 & C-6),
	3.64 (s, 6H, ax-OCH ₃), 3.92 (dd, 4H, H _M , J _{AM} = 10.7 Hz), 4.30 (dd, 4H, H _A), 7.08-7.19 (m, 14H, Ar-H)	66.2 (C-4), 175.8 (C=O)
4b	2.35 (s, 6H, CH ₃), 2.94 (dd, 4H, H_X , J_{AX} = 5.5, J_{MX} = 15.8 Hz), 3.55 (s, 6H, eq-OCH ₃), 3.64 (s, 6H, ax-OCH ₃), 3.93 (dd, 4H, H_M , J_{AM} = 10.5 Hz), 4.28 (dd, 4H, H_A), 6.97-7.13 (m, 12H, Ar-H)	20.5 (CH ₃), 27.9 (C-3 & C-5), 49.6 & 50.8 (OCH ₃), 55.9 (C-2 & C-6), 66.7 (C-4), 177.3 (C=O)
4c	2.93 (dd, 4H, H_X , J_{AX} = 5.3, J_{MX} = 15.9 Hz), 3.56 (s, 3H, eq-OCH ₃), 3.66 (s, 3H, ax-OCH ₃), 3.94 (dd, 4H, H_M , J_{AM} = 10.6 Hz), 4.28 (dd,	28.1 (C-3 & C-5), 50.2 & 51.9 (OCH ₃), 55.9 (C-2 & C-6), 67.2 (C-4), 174.9 (C=O)
5a	4H, H_A), 7.05-7.19 (m, 12H, Ar-H) 1.32 (t, 6H, OCH2C H_3), 2.92 (dd, 4H, H_X , J_{AX} = 5.4, J_{MX} = 15.8 Hz), 3.93 (dd, 4H, H_M , J_{AM} = 10.4 Hz), 4.12 (q, 4H, OC H_2 C H_3), 4.30 (dd,	13.6 (OCH ₂ CH ₃), 28.0 (C-5), 28.3 (C-3), 55.5 (C-2 & C-6), 58.3 (C-4), 59.3 (OCH ₂ CH ₃), 119.2 (CN), 176.0 (C=O)
5b	4H, H _A), 6.93-7.19 (m, 14H, Ar-H) 1.30 (t, 6H, OCH ₂ CH ₃), 2.37 (s, 6H, CH ₃), 2.96 (dd, 4H, H _X , J_{AX} = 5.5, J_{MX} = 15.8 Hz), 3.93 (dd, 4H, H _M , J_{AM} = 10.7 Hz), 4.11 (q,	13.7 (OCH ₂ CH ₃), 20.6 (CH ₃), 27.5 (C-5), 29.2 (C-3), 54.9 (C-2 & C-6), 57.4 (C-4), 58.9 (OCH ₂ CH ₃), 120.4 (CN), 178.3 (C=O)
5c	4H, OC H_2 CH ₃), 4.29 (dd, 4H, H _A), 6.94-7.12 (m, 12H, Ar-H) 1.33 (t, 6H, OCH ₂ CH ₃), 2.93 (dd, 4H, H _X , J_{AX} = 5.5, J_{MX} = 15.7 Hz), 3.95 (dd, 4H, H _M , J_{AM} = 10.6 Hz), 4.14 (q, 4H, OC H_2 CH ₃), 4.31 (dd, 4H, H _A), 6.94-7.21 (m, 12H, Ar-H)	13.5 (OCH ₂ CH ₃), 28.4 (C-5), 28.9 (C-3), 56.0 (C-2 & C-6), 59.3 (C-4), 59.5 (OCH ₂ CH ₃), 118.9 (CN), 175.8 (C=O)
6a	1.31 (t, 6H, OCH ₂ CH ₃), 2.91 (dd, 4H, H _X , J_{AX} = 5.3, J_{MX} = 15.7 Hz), 3.94 (dd, 4H, H _M , J_{AM} = 10.4 Hz), 4.09 (q, 4H, OCH ₂ CH ₃), 4.34 (dd, 4H, H _A), 7.05-7.21 (m, 14H, Ar-H)	13.7 (OCH ₂ CH ₃), 27.8 (C-3 & C-5), 55.9 (C-2 & C-6), 58.4 (C-4), 59.7 (OCH ₂ CH ₃), 118.7 (CN), 174.3 (C=O)
6b	1.33 (t, 6H, OCH ₂ CH ₃), 2.36 (s, 6H, CH ₃), 2.93 (dd, 4H, H_X , J_{AX} = 5.3, J_{MX} = 15.9 Hz), 3.97 (dd, 4H, H_{M} , J_{AM} = 10.6 Hz), 4.11 (q, 4H, OCH ₂ CH ₃), 4.31 (dd, 4H, H_A), 6.96-7.12 (m, 12H, Ar-H)	13.4 (OCH ₂ CH ₃), 20.4 (CH ₃), 28.3 (C-3 & C-5), 56.3 (C-2 & C-6), 58.9 (C-4), 59.5 (OCH ₂ CH ₃), 118.2 (CN), 173.9 (C=O)
6c	$\begin{array}{l} 1.30~({\rm t,6H,OCH_2C}H_3),2.91~({\rm dd,4H,H_X},J_{AX}\!=5.2,J_{MX}\!=15.9~{\rm Hz}),\\ 3.94~({\rm dd,4H,H_M},J_{AM}\!=10.4~{\rm Hz}),4.13~({\rm q,4H,OC}H_2{\rm CH_3}),4.33~({\rm dd,H_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_$	13.7 (OCH ₂ CH ₃), 27.8 (C-3 & C-5), 55.9 (C-2 & C-6), 58.6 (C-4), 59.5 (OCH ₂ CH ₃), 119.6 (CN), 174.2 (C=O)
7a	4H, H_A), 7.03-7.22 (m, 12H, Ar-H) 2.93 (dd, 4H, H_X , J_{AX} = 5.5, J_{MX} = 15.7 Hz), 3.94 (dd, 4H, H_M , J_{AM} = 10.6 Hz), 4.32 (dd, 4H, H_A), 6.96-7.21 (m, 14H, Ar-H)	28.1 (C-5), 28.4 (C-3), 54.8 (C-2 & C-6), 58.2 (C-4), 119.2 & 121.8 (CN)
7b	2.35 (s, 6H, CH ₃), 2.94 (dd, 4H, H _X , J_{AX} = 5.3, J_{MX} = 15.8 Hz), 3.97 (dd, 4H, H _M , J_{AM} = 10.5 Hz), 4.31 (dd, 4H, H _A), 6.95-7.14 (m, 12H, Ar-H)	20.6 (CH ₃), 28.3 (C-5), 28.9 (C-3), 55.8 (C-2 & C-6), 58.0 (C-4), 118.2 & 121.6 (CN)
7c	2.92 (dd, 4H, H_X , J_{AX} = 5.5, J_{MX} = 15.7 Hz), 3.93 (dd, 4H, H_M , J_{AM} = 10.7 Hz), 4.34 (dd, 4H, H_A), 6.94-7.22 (m, 12H, Ar-H)	28.8 (C-5), 29.7 (C-3), 54.9 (C-2 & C-6), 59.6 (C-4), 119.4 & 121.2 (CN)
8a	2.91 (dd, 4H, H_X , $J_{AX} = 5.3$, $J_{MX} = 15.8$ Hz), 3.95 (dd, 4H, H_M , $J_{AM} = 10.4$ Hz), 4.33 (dd, 4H, H_A), 7.03-7.20 (m, 14H, Ar-H)	28.4 (C-3 & C-5), 54.5 (C-2 & C-6), 58.9 (C-4), 118.8 & 120.6 (CN)
8b	2.34 (s, 6H, CH ₃), 2.93 (dd, 4H, H _X , J_{AX} = 5.5, J_{MX} = 15.7 Hz), 3.96 (dd, 4H, H _M , J_{AM} = 10.5 Hz), 4.32 (dd, 4H, H _A), 6.98-7.11 (m, 12H, Ar-H)	20.2 (CH ₃), 27.9 (C-3 & C-5), 55.3 (C-2 & C-6), 58.6 (C-4), 119.2 & 120.8 (CN)
8c	2.94 (dd, 4H, H_X , J_{AX} = 5.3, J_{MX} = 15.8 Hz), 3.95 (dd, 4H, H_M , J_{AM} = 10.7 Hz), 4.31 (dd, 4H, H_A), 7.02-7.20 (m, 12H, Ar-H)	28.6 (C-3 & C-5), 55.3 (C-2 & C-6), 58.5 (C-4), 117.2 & 120.8 (CN)

nals for methylene, methine and tertiary carbons in the regions δ 54.5-56.4, 27.9-28.9 and 58.2-68.0, respectively, however the compounds **3-4** exhibited signals at δ 49.9-50.7, 51.7-52.8 which are assigned to magnetically nonequivalent carbonyl carbons of carbomethoxy groups. Compounds **5** and **6** also displayed signals at δ 59.3-59.7 for carbonyl carbon of carboethoxy group. On the other hand, compounds **7** and **8** showed signal characteristic to CN group at δ 117.2-119.2 and 120.6-121.8, respectively.

EXPERIMENTAL

Melting points were determined in open capillaries on a MelTemp apparatus, and the purity of the compounds was checked by TLC (silica gel H, BDH, ethyl acetate/hexane, 3:1). The IR spectra were recorded on a Perkin-Elmer grating infrared spectrophotometer, model 337 in KBr pellets. $^1\mathrm{H}$ NMR spectra for compounds 1 and 2 were recorded in DMSO- d_6 and for compounds 3-8 in CDCl $_3$ using 300 MHz on a Varian EM-360 spectrophotometer. $^{13}\mathrm{C}$ NMR spectra were recorded on a Varian VXR spectrometer operating at 75.5 MHz. All chemical shifts were reported in ppm from TMS as an internal standard. The elemental analyses were performed at Punjab University, Chandigarh, India.

General Method of the Synthesis of 1,3-Bis-[2-(2-arylethenesulfonyl)-vinyl]-benzenes **1a-c** and 1,4-Bis-[2-(2-arylethenesulfonyl)-vinyl]-benzenes 2a-c.

A solution of 2 mmol of 2-arylethenesulfonylacetic acid in 10 mL of glacial acetic acid is mixed with 1 mmol of 1,3- or 1,4-benzenedicarboxaldehyde and 0.2 mL of benzylamine and refluxed for 6-8 hours. The reaction mixture is cooled, treated with 50 mL of dry ether and refrigerated overnight. Any product separated is collected by filtration. The filtrate is diluted with 20 mL of ether and washed successively with 20 mL of a saturated solution of sodium bicarbonate, 20 mL of sodium bisulphite, 20 mL of dilute hydrochloric acid and finally with 35 mL of water. Evaporation of the dried ethereal layer gave a solid product, which is purified by recrystallization from 2-propanol.

General Method of the Synthesis of Dimethyl 3,3'-(1,3-Phenylene)-bis-(5-aryl-tetrahydro-4*H*-thiopyran-4,4-dicarboxylate 1,1-Dioxides) (**3**), Dimethyl 3,3'-(1,4-Phenylene)-bis-(5-aryl-tetrahydro-4*H*-thiopyran-4,4-dicarboxylate 1,1-Dioxides) (**4**), Ethyl 3,3'-(1,3-Phenylene)-bis-(5-aryl-4-cyanotetrahydro-2*H*-thiopyran-4-carboxylate 1,1-Dioxides) (**5**), Ethyl 3,3'-(1,4-

Phenylene)-bis-(5-aryl-4-cyanotetrahydro-2*H*-thiopyran-4-carboxylate 1,1-Dioxides) (**6**), 3,3'-(1,3-Phenylene)-bis-(5-aryl-tetrahydro-4*H*-thiopyran-4,4-dicarbonitrile 1,1-Dioxides) (**7**) and 3,3'-(1,4-Phenylene)-bis-(5-aryl-tetrahydro-4*H*-thiopyran-4,4-dicarbonitrile 1,1-Dioxides) (**8**).

To a solution of 1 mmol of the appropriate bis-[2-(2-arylethenesulfonyl)-vinyl]-benzenes 1 or 2 and 3 mmol of dimethyl malonate, ethyl cyanoacetate or malononitrile in 10 mL of tetrahydrofuran, a catalytic amount of Triton-B is added and refluxed for 3-6 hours. The reaction mixture is cooled and the solvent is removed under reduced pressure. The syrupy substance obtained is solidified on treatment with methanol or 2-propanol. The resultant compound is passed through a column of silica gel (60-120) mesh, BDH, with hexane/ethyl acetate (3:1) as eluents.

REFERENCES AND NOTES

- * To whom correspondence should be addressed: Email: vkpuram2001@yahoo.com
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