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CONDENSATION PRODUCTS OF MONO- AND DIBROMO-SUBSTITUTED METHYL VINYL SULFONES WITH CH-ACIDS ENOLATES

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Bromomethyl (E)-2-phenylethenyl and bromomethyl (Z)-1-bromo-2-phenylethenyl sulfones undergo condensation with enolates generated from malononitrile, dimethyl malonate, methyl and ethyl acetoacetate using NaH in THF to give tetrahydrothiophene S,S-dioxides. Methyl (E)-1-bromo-2-phenylethenyl and methyl (E)-2-bromo-2-phenylethenyl sulfones react with sodium malononitrile to give 2-[2-(methylsulfonyl)-1-phenylethylidene]malononitrile. The bromomethyl-(E)-2-bromo-2-phenyl ethenyl sulfone reacts with sodium malononitrile to give 2-[2-(bromomethylsulfonyl)-1-phenylethylidene]malononitrile exclusively.

Keywords: CH-acids enolates, tetrahydrothiophene-S,S-dioxide, 2-phenylethenyl sulfones, ethylidene-malononitrile, heterocyclization, Michael reaction, Ramberg-Bäcklund reaction.

It is known [1, 2] that bromomethyl vinyl sulfones and, in particular, the sulfone **1a** undergo a Michael induced Ramberg-Bäcklund (MIRB) addition reaction when treated with sodium alcoholate to give alkyl allyl ethers. Benzyl α-bromovinyl sulfone reacts with different nucleophiles by a similar scheme to give allyl derivatives [3]. As members of the series of α-bromovinyl bromomethyl and β-bromovinyl bromomethyl sulfones the dibromosulfones **2a** and **3a** also react *via* an MIRB reaction with sodium methylate, presumably through a bromomethyl ethynyl sulfone stage to form a vinyl phenyl ketone dimethyl ketal in both cases [2]. It is also known that some α-bromovinyl sulfones unable to take part in the Ramberg-Bäcklund reaction cyclize to sulfonyl-substituted aziridine derivatives when treated with primary amines in DMSO [4]. Similarly, several α-chlorovinyl sulfones not able to undergo the Ramberg-Bäcklund reaction undergo Michael induced addition cyclization to give sulfonyl-substituted dihydrofuran and cyclopropane derivatives when treated with ethylacetoacetate or diethyl malonate enolates [5].

The examples given point to a variety of reactions of halo-substituted methyl vinyl sulfones in Michael induced addition reactions and open up a short route to the formation of acyclic, cyclic, and heterocyclic structures difficult to prepare by other methods.

In this work we have studied the reactions of mono- and dibromo-substituted methyl vinyl sulfones with CH-acids enolates with a view to determining the effect of the position and number of bromine atoms on the

Dedicated to Professor A. A. Potekhin's memory.

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TABLE 1. Characteristics of Compounds Synthesized

Compound	Compound name	Empirical formula	Found, % / Calculated, %			mp, °C*	Yield, %
			C	H	N		
1b	Methyl (*E*)-2-phenylethenyl sulfone	$C_9H_{10}BrO_2S$	59.45 / 59.32	5.32 / 5.53		79-80	86
2b	Methyl (*Z*)-1-bromo-2-phenylethenyl sulfone	$C_9H_9BrO_2S$	41.52 / 41.40	3.56 / 3.47		78-79	80
3b	Methyl (*E*)-2-bromo-2-phenylethenyl sulfone	$C_9H_9BrO_2S$	41.37 / 41.40	3.34 / 3.47		66-67	35
4b	Methyl 2-bromo-2-phenylethyl sulfone	$C_9H_{11}BrO_2S$	40.97 / 41.08	4.33 / 4.21		119-120	55
5b	*threo* Methyl 1,2-dibromo-2-phenylethyl sulfone	$C_9H_{10}Br_2O_2S$	31.71 / 31.60	3.07 / 2.95		130-131	10*[2]
6a	1,1-Dioxo-4-phenyltetrahydrothiophene-3,3-dicarbonitrile	$C_{12}H_{10}N_2O_2S$	58.54 / 58.52	4.09 / 4.09	11.45 / 11.37	236-237	70
6b	Dimethyl 1,1-dioxo-4-phenyltetrahydrothiophene-3,3-dicarboxylate	$C_{14}H_{16}O_6S$	53.79 / 53.84	5.24 / 5.16		130-131	54
6c	*trans*-3-Acetyl-*cis*-3-ethoxycarbonyl-1,1-dioxo-4-phenyltetrahydrothiophene	$C_{15}H_{18}O_5S$	58.11 / 58.05	5.82 / 5.85		145-146	49
6d	*trans*-3-Acetyl-*cis*-3-methoxycarbonyl-1,1-dioxo-4-phenyltetrahydrothiophene	$C_{14}H_{16}O_5S$	56.83 / 56.74	5.65 / 5.44		160-161	53
7	Bromo-4-phenyldihydro-3,3(2H)-thiophenedicarbonitrile 1,1-dioxide	$C_{12}H_9BrN_2O_2S$	44.38 / 44.32	2.86 / 2.79	8.52 / 8.61	237-238	51
9a	2-[2-(Bromomethylsulfonyl)phenylethylidene]malononitrile	$C_{12}H_9BrN_2O_2S$	44.27 / 44.32	2.83 / 2.79	8.83 / 8.61	143-144	65
9b	2-[2-(Methylsulfonyl)-1-phenylethylidene]malononitrile	$C_{12}H_{10}N_2O_2S$	58.43 / 58.52	4.16 / 4.09	11.28 / 11.37	120-121	34
11	(2,2-Dimethoxy-2-phenylethyl) methyl sulfone	$C_{11}H_{16}O_4S$	54.16 / 54.08	6.63 / 6.60		117-118	79
12	2-(Methylsulfonyl)-1-phenyl-1-ethanone	$C_9H_{10}O_3S$	54.27 / 54.53	5.18 / 5.08		105-106	70

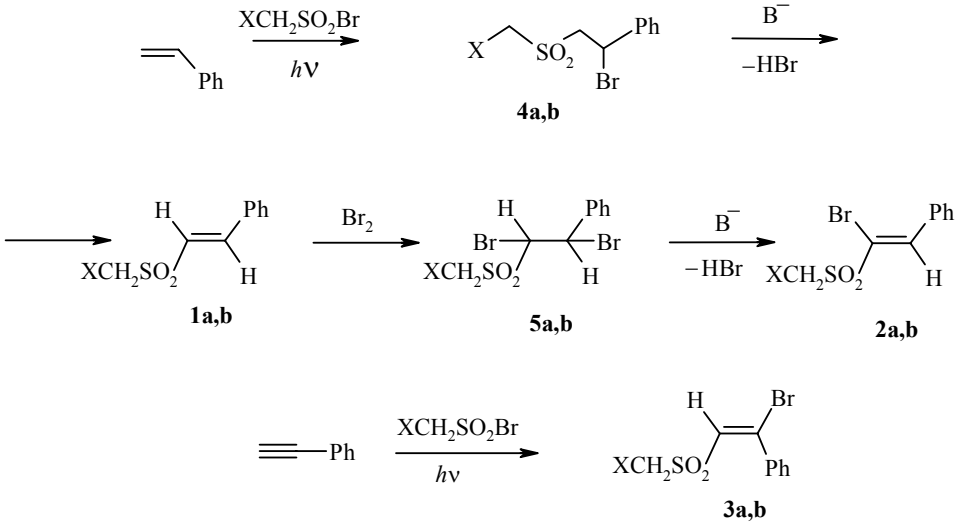
* Solvent: $CHCl_3$–CCl_4, 1:2 (compounds **1b, 3b, 4b, 5b, 6b, 9b, 11, 12**), CH_2Cl_2 (compound **2b**), ether–hexane, 1:3 (compounds **6c,d**), dioxane-ether, 1:1 (compound **6a**), ethyl acetate–hexane, 1:1 (compounds **7, 9a**).

*[2] Together with *erythro*-**5b** = 50%

TABLE 2. Mass Spectra of the Compounds Synthesized

Compound	*m/z* (*I*, %)
2b	262 (12.9)/260 (12.9) $[M]^{+\bullet}$, 183 (9)/182 (79)/181 (24)/180 (81), 171 (7.2)/169 (7.7), 102 (100), 90 (10), 89 (9.7), 76 (19), 75 (12), 63 (12)
7	326 (3)/324 (3) $[M]^{+\bullet}$, 184 (98)/182 (100), 104 (36)/103 (71)/102 (25), 77 (60), 51 (43)
9b	248 (1.6)/246 (29.6) $[M]^{+\bullet}$, 181 (8), 169 (10), 168 (84), 167 (40.5), 142 (10), 141 (19), 140 (100), 127 (7), 114 (10), 113 (13), 103 (8), 102 (5), 79 (54), 78 (5), 77(21), 65 (4), 64 (7), 63 (12), 51 (23)
12	200 (0.3)/198 (5) $[M]^{+\bullet}$, 106 (7)/105 (100), 91 (9), 79 (2.7)/78 (3.5)/77 (34), 63 (2.7), 51 (13)

realization of one or the other possible routes for their reaction. We have chosen the bromomethyl vinyl sulfone **1a** and bromomethyl bromovinyl sulfones **2a** and **3a** mentioned above together with the methyl bromovinyl sulfones **2b** and **3b** as the subject of our investigation (Tables 1-3).



1–5 a X = Br, **b** X = H

The starting materials **2a,b** were prepared from the styrene photoadducts **4a,b** respectively with bromomethane- and methanesulfobromides. To do this the adducts **4a,b** were treated with an aqueous dioxane solution of Na_2CO_3 at 20ºC giving initially the sulfones **1a,b** which were treated with bromine in CCl_4 at 20ºC to give the dibromides **5a,b**. The dibromides **5a** and **5b** were then dehydrobrominated by heating in aqueous dioxane Na_2CO_3 solution at 50ºC to give the sulfones **2a** and **2b** respectively. Compounds **3a** and **3b** were prepared by the photochemical addition of bromomethane- and methanesulfobromide to phenylacetylene.

Detailed methods for the synthesis and proof of the structure of sulfones **1a-3a** have been given by us in [2]. The sulfones **1b** [2] and **3b** [6] were identified from the constants and spectroscopic parameters reported in the literature. It was notable that the dibromosulfone **5b**, which was obtained as a *threo* / *erythro* isomer mixture, gave exclusively on dehydrobromination the unsaturated sulfone **2b**, the configuration of which was confirmed by reduction with zinc dust in acetic acid to the sulfone **1b**. We have previously observed a similar reaction for the dibromosulfone **5a** [2].

TABLE 3. IR Spectra of the Compounds Synthesized*

Com-pound	Characteristic frequencies, ν, cm^{-1}
1b	509 s, 687 m, 744 s, 760 s, 798 m, 972 s, 1115 s, 1138 s, 1277 vs, 1451 m, 1624 m, 2928 w, 3028 w, 3048 m
2b	513 s, 528 s, 586 m, 694 s, 748 m, 760 s, 972 s, 1138 vs, 1308 vs, 1442 m, 1485 m, 1605 m, 2928 w, 3008 w, 3024 w
3b	509 s, 702 s, 779 s, 964 s, 1130 vs, 1292 s, 1319 s, 1628 m, 2924 w, 3009 w, 3048 m
4b	459 m, 509 s, 698 s, 775 m, 914 s, 1119 vs, 1269 s, 1304 vs, 1323 s, 1454 m, 2928 w, 2978 w
treo-**5b**	436 m, 513 m, 702 s, 833 s, 952 s, 953 m, 1119 s, 1300 vs, 1312 s, 1454 m, 1493 m, 2928 m, 2978 w
6a	529 s, 700 s, 770 m, 1140 vs (SO_2, ν_s), 1231 m, 1262 s, 1306 s (SO_2, ν_{as}), 1339 s, 2253 w (CN), 2967 m, 3029 m
6b	706 m, 789 m, 1120 s (SO_2, ν_s), 1146 m, 1236 m, 1310 s (SO_2, ν_{as}), 1434 m, 1728 vs (C=O), 1747 s (C=O), 2960 w, 3012 w
6c	702 m, 1124 s, 1155 s (SO_2, ν_s), 1248 s, 1309 s (SO_2, ν_{as}), 1330 s, 1368 w, 1712 vs (C=O), 1734 m (C=O), 3002 w
6d	455 m, 706 m, 889 w, 1124 s, 1157 w, 1250 s, 1310 m, 1331 w, 1717 vs, 1738 m, 2955 w, 3002 w
7	490 m, 540 m, 695 m, 702 m, 772 m, 1142 s, 1262 m, 1323 m, 1343 vs, 1458 w, 1501 w, 2260 vw, 2955 m, 2978 s, 3017 m
9a	478 m, 494 m, 837 m, 1103 m, 1138 s, 1211 m, 1308 m, 1325 vs, 1555 m, 1593 w, 1632 w, 2234 m, 2930 w, 2951 m, 2994 w, 3021 w
9b	482 m, 513 m, 536 m, 702 m, 737 m, 795 s, 972 s, 1142 vs, 1149 s, 1315 vs, 1427 m, 1446 m, 1566 m, 1585 w, 2233 m, 2935 w, 3020 w
11	475 m, 521 m, 706 m, 787 m, 957 m, 1046 m, 1103 s, 1146 s, 1308 vs, 1416 m, 1447 m, 1559 w, 2924 w, 2955 m, 3025 w
12	498 m, 583 m, 753 m, 768 m, 961 m, 1103 m, 1119 m, 1154 s, 1219 m, 1285 s, 1304 vs, 1451 m, 1678 s

* Ten strongest and characteristic absorption bands are quoted

The CH-acids enolates were generated using NaH in THF at 20-45ºC under a dry argon atmosphere. The broadest range of CH-acids was used in the condensation reactions with bromomethyl vinyl sulfone **1a** (dimethylmalonate, malononitrile, methyl and ethyl acetoacetate). The remaining mono- and dibromosulfones were only studied using the malononitrile enolate.

Independently of the nature of the CH-acids the single reaction product of the reaction of the sulfone **1a** was the corresponding heterocyclization product **6a-d***[2] in every case.

The differences in the H-4 and 2H-5 signals in the ^{1}H NMR spectra of compounds **6a-d** (Table 4) deserve attention. Whereas in the case of the heterocycle **6a** the expected ABX type multiplet is observed, for compounds **6c,d** a degenerate ABX multiplet is seen (approximating to the AA'X type, virtual spin-spin couplings are given in Table 4, see [8, 9]) and this is due to the closeness of the chemical shifts of the H-5 protons and the high geminal spin spin coupling constant. The exchange of $CDCl_3$ solvent to C_6D_6 causes a change in the signal chemical shifts in the ^{1}H NMR spectrum of compound **6d** but the form of the discussed multiplet remains as earlier: a doublet at 3.13 (J = 8.0 Hz) and triplet at 4.57 ppm (J = 7.3 Hz). The corresponding signal for compound **6b** has an intermediate form: in the X part it appears as a triplet (virtual spin-spin coupling given in Table 4) and in the AB part it is more complex than a doublet, being a multiplet with one of the H-2 proton signals superimposed.

*[2] Part of this material has been reported in [7].

TABLE 4. ^{1}H and ^{13}C NMR Spectra of Compounds **6a-d**, **7**

Compound	Chemical shifts, δ, ppm (*J*, Hz)												
	^{1}H NMR spectrum						^{13}C NMR spectrum						
	syn-H-2*, d	*anti*-H-2, d	H-4	*syn*-H-5	*anti*-H-5	CO_2R [$COCH_3$]	C-2	C-3	C-4	C-5	C=O (CN)	COR	Ph
6a[*2]	4.34 (*J* = 13.1)	4.59 (*J* = 13.1)	4.65 (dd, *J* = 7.3 and *J* = 12.4)	3.98 (dd, *J* = 13.1 and *J* = 13.8)	4.06 (dd, *J* = 8.0 and *J* = 13.8)	—	57.7	39.9	52.2	47.8	(112.4, 112.8)	—	128.7 (2C), 129.1 (2C), 129.8, 132.0
6b	3.67 (*J* = 14.0)	4.05 (*J* = 14.0)	4.66 (t, *J* = 7.3)	3.60-3.70 (m)		3.42 (s), 3.86 (s)	56.0[*3]	61.7	45.7	55.1[*3]	166.9, 168.5	53.1, 53.9	128.3 (2S), 128.5, 128.8 (2S), 136.2
6c	3.48 (*J* = 14.3)	4.10 (*J* = 14.3)	4.66 (t, *J* = 7.2)	3.62 (d, *J* = 7.6)		1.02 (t, *J* = 7.6), 3.78 (dq, *J* = 7.6, *J* = 10.9), 3.98 (dq, *J* = 7.6, *J* = 10.9), [2.26, s]	56.0	67.3	44.1	54.2	166.8, 198.4	13.0, 26.3, 62.6	128.3, 128.4 (2C), 128.8 (2C), 136.6
6d	3.49 (*J* = 14.5)	4.08 (*J* = 14.5)	4.67 (t, *J* = 7.3)	3.62 (d, *J* = 7.3)		3.46 (s), [2.26 (s)]	56.2	67.6	44.3	54.3	167.4, 198.4	26.5, 53.1	128.3, 128.4 (2C), 128.9 (2C), 136.6
7	3.95 (*J* = 13.8)	4.25 (*J* = 13.8)	5.36 (d, *J* = 13.1)	4.00 (d, *J* = 13.1)	—	—	57.7	37.9	56.5	58.2	(110.8, 111.1)	—	127.8, 128.4 (2C), 130.0 (2C), 131.3

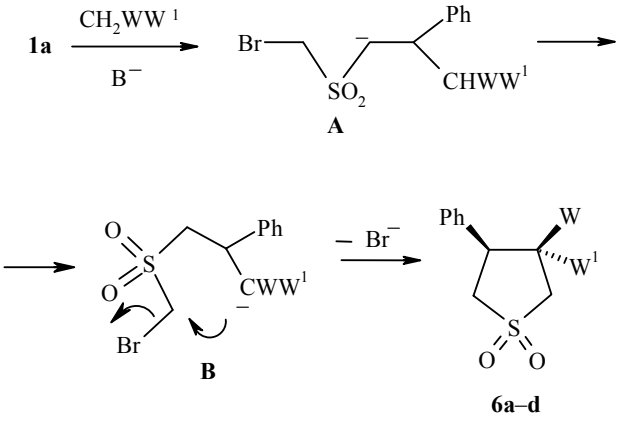
* *Syn* and *anti* positions relate to the phenyl substituent.

*[2] Solvent DMSO-d_6.

*[3] Assigned signals may be reversed.

TABLE 5. ^{1}H and ^{13}C NMR Spectra of Compounds **2-5**, **9, 11, 12**

Com-pound	Chemical shifts, δ,ppm. (*J*, Hz)	
	^{1}H NMR Spectra	^{13}C NMR Spectra
2b	3.16 (3H, s, CH_3); 7.43-7.53 (3H, m, H_{arom}), 7.81-7.90 (2H, m, H_{arom}).; 8.21 (1H, s, vinyl proton)	39.6 (CH_3); 119.3, 128.7 (2C); 130.1 (2C); 131.2, 131.5 and 139.5 (C_{arom} and C_{olef})
3b	2.75 (3H, s, CH_3); 7.12 (1H, s, vinyl proton); 7.40-7.50 (3H, m, H_{arom}); 7.51-7.59 (2H, m, H_{arom})	43.2 (CH_3); 128.4 (2C); 128.6 (2C); 131.0, 133.1, 135.8 and 139.1 (C_{arom} and C_{olef})
4b	2.57 (3H, s, CH_3); 3.95 (2H, d, *J* = 7.4, CH_2); 5.42 (1H, t, *J* = 7.4, CHBr); 7.38-7.58 (5H, m, H_{arom})	42.4 (CH_3); 43.9 (CH_2); 63.7 (CHBr); 127.6 (2C); 129.3 (2C); 129.6 and 139.0 (C_{arom})
treo-**5b**	2.60 (3H, s, CH_3); 5.31 (1H, d, *J* = 4.4, methine proton); 5.81 (1H, d, *J* = 4.4, methine protons); 7.38-7.46 (3H, m, H_{arom}); 7.63-7.72 (2H, m, H_{arom})	38.8 (CH_3); 47.0 (<u>C</u>Ph); 70.2 (CSO_2); 128.5 (2C); 129.6 (2C); 130.0 and 135.3 (C_{arom})
eritro-**5b**	3.20 (3H, s, CH_3); 4.94 (1H, d, *J* = 2.5, methine proton) and 5.86 (1H, d, *J* = 2.5, methine proton); 7.37-7.44 (3H, m, H_{arom}); 7.52-7.60 (2H, m, H_{arom})	39.2 (CH_3); 49.8 (<u>C</u>Ph); 70.4 (CSO_2); 128.1 (2C); 128.7 (2C); 129.9 and 136.9 (C_{arom})
9a	4 .16 (2H, s, CH_2Br); 4.85 (2H, s, CH_2); 7.58-7.71 (5H, m, H_{arom})	42.9 (CH_2Br); 56.7 (CH_2); 91.4 (<u>C</u>Ph); 111.6 and 111.8 (CN); 128.2 (2C); 129.8 (2C); 132.7 and 133.5 (C_{arom}); 162.6 (<u>C</u>$(CN)_2$)
9b	2.88 (3H, s, CH_3); 4.65 (2H, s, CH_2); 7.55-7.69 (5H, m, H_{arom})	42.8 (CH_3); 61.5 (CH_2); 90.3 (<u>C</u>Ph); 111.9 and 112.2 (CN); 128.2 (2C); 129.6 (2C); 133.2 and 133.3 (C_{arom}); 163.7 (<u>C</u>$(CN)_2$)
11	2.26 (3H, s, CH_3); 3.27 (6H, s, OCH_3); 3.69 (2H, s, CH_2); 7.38-7.48 (3H, m, H_{arom}); 7.61 (2H, d, *J* =8.0, H_{arom})	41.8 (CH_3); 49.0 (2S, OCH_3); 60.6 (CH_2); 99.4 (<u>C</u>$(OCH_3)_2$); 127.3 (2C); 128.5 (2C); 129.0 and 137.9 (C_{arom})
12	3.17 (3H, s, CH_3); 4.63 (2H, s, CH_2); 7.54 (2H, t, *J* = 7.5, H_{arom}); 7.68 (1H, t, *J* = 7.5, H_{arom}); 8.02 (2H, d, *J* = 8.0, H_{arom})	41.7 (CH_3); 61.2 (CH_2); 129.0 (2C); 129.2 (2C); 134.6 and 135.6 (C_{arom}); 189.1 (C=O)



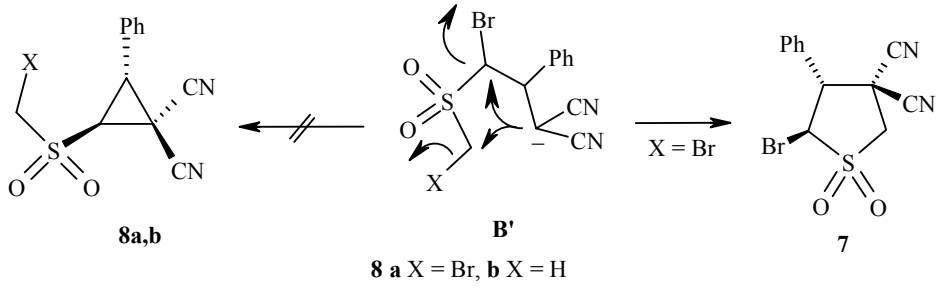
6 a W = W^1 = CN; **b** W = W^1 = CO_2Me; **c** W = CO_2Et, W^1 = COMe; **d** W = CO_2Me, W^1 = COMe

It was notable that each of the compounds **6c** and **6d** is formed exclusively as one of two possible diastereomers, in fact with a *cis* orientation of the phenyl and ester groups. The configuration of the diastereomers was established on the basis of a comparison of the chemical shifts of the methoxycarbonyl protons in the ^{1}H NMR spectra of compounds **6b** and **6d**. The singlet signals of the two non-equivalent CO_2Me groups in heterocycle **6b** were markedly removed one from the other and the signal corresponding to the group shielded by the phenyl substituent (3.42 ppm) was virtually coincident with the chemical shift of the methoxycarbonyl proton signal (3.46 ppm) in heterocycle **6d**.

We explain the formation of compounds **6a-d** in terms of initial Michael addition to give carbanion **A** with transfer of a proton to form the more stable carbanion **B** (see [5]). The latter can take part in a 1,5-cyclization to form the tetrahydrothiophene S,S-dioxide. The strict stereoslectivity of the reacrions chemistry involving the acetoacetate deserves discussion. Although the van der Waal radius of the CO_2Me group (1.62 Å [10]) somewhat exceeds that of the COMe group (1.56 Å), in the transition state (in which the carbon atom bonded to this substituent carries a marked negative charge) the effective steric volume of the indicated groups can be significantly different. In fact, because the acetyl group is a considerably more powerful π-acceptor than the carbalkoxy group it delocalizes the electron density better and this leads to an inhibition of its rotation around the C–C bond and hence simultaneously to an increase in the effective steric bulk when compared with a similar but more mobile carbalkoxy group. Hence the latter in fact proves to be in a *cis* position to the phenyl substituent in the transition state and in the reaction product.

Condensation of dibromide **2a** with sodium malononitrile gave the corresponding heterocyclic monobromide **7**. The ^{13}C NMR spectrum of bromide **7** (Table 4) is in the expected agreement with that of the analogous **6a**. Comparison of the ^{1}H NMR spectra of compound **7** and **6a** shows a strong difference in the chemical shifts of the H-4 proton and a virtually identical position for the H-5 proton signals. Hence we can conclude that the bromide **7** has a *trans* configuration with the known shielding effect of a phenyl ring and deshielding effect of a bromine atom on oppositely placed vicinal protons.

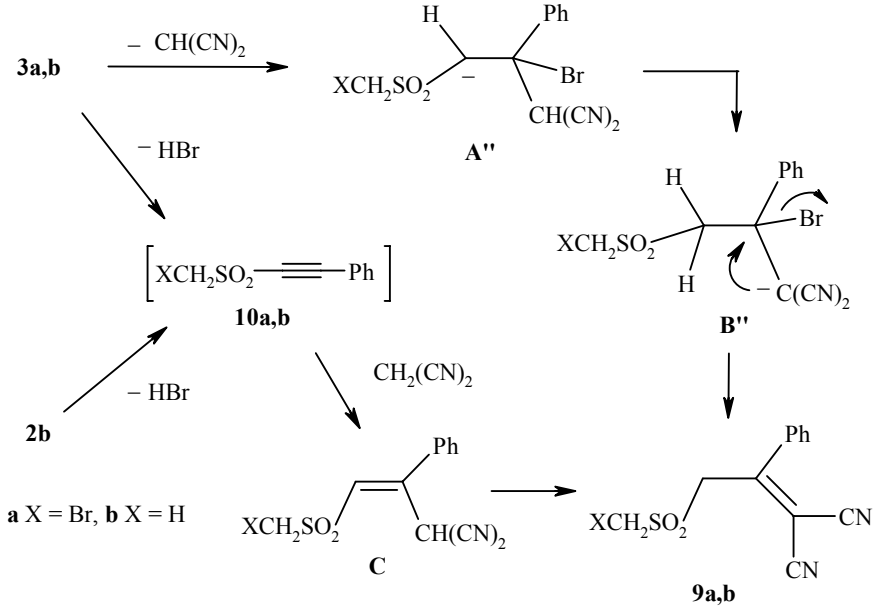
Formation of heterocycle **7** can be rationalized by a scheme analogous to formation of compounds **6**, in fact a 1,5-cyclization of carbanion **B'**. Hence the presence of the vinyl bromine atom in compound **2a** does not change the direction of its reaction when compared with the sulfone **1a**. For carbanion **B'** another type of reaction could *a priori* be possible, i.e. a 1,3-cyclization, the result of which would be the formation of the cyclopropane **8a**. However, this is not realized, evidently because the 1,5-cyclization route proves to be more favored.



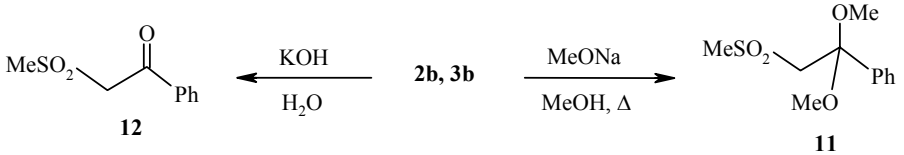
8 a X = Br, **b** X = H

For the methyl α-bromovinyl sulfone **2b** unable to take part in a 1,5-cyclization, the main Michael induced addition reaction route for sodium malononitrile might prove to be a 1,3-cyclization leading to the cyclopropane **8b**. However only the ethylidenemalononitrile derivative **9b** is in fact formed.

Treatment of the β-bromovinyl sulfones **3a** and **3b** with sodium malononitrile gives exclusively the ethylidenemalononitrile derivatives **9a** and **9b** respectively.



Formation of these compounds from sulfones **3a,b** might be explained as a Michael addition induced 1,2-dihydrobromination involving carbanions **A''** and **B''**. However a more likely alternative route would be initial dehydrobromination of bromides **3a,b** to the ethynyl sulfones **10a,b**, subsequent Michael addition of the malononitrile, and prototropic isomerization of the adduct **C**. An experimental conversion of the specifically synthesized ethynyl sulfone **10b** to compound **9b** under similar conditions served to support this hypothesis. Finally, formation of the ethylidenemalononitrile **9b** from the α-bromovinyl sulfone **2b** can occur only *via* an initial dehydrobromination with the intermediate formation of the same ethynyl sulfone **10b**. The fact that both the 1-bromovinyl sulfone **2b** and the 2-bromovinyl sulfone **3b** are liable to dehydrobromination to form the same ethynyl sulfone **10b**, active in a nucleophilic addition reaction, was identified by treating them with stronger basic nucleophiles than sodium malononitrile, in fact sodium methylate in methanol and water–alcohol alkali. The dimethyl ketal **11** was obtained in the first case and the ketone **12** in the second.



EXPERIMENTAL

Elemental analysis was carried out on an HP-185B CHN analyzer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-300 spectrometer (300 and 75 MHz) using $CDCl_3$ and the chemical shifts in the ^{1}H NMR spectra were measured relative to the residual solvent signal at 7.26 ppm or for compound **6a** relative to the residual DMSO-d_6 signal at 2.50 ppm as the internal standards. IR spectra were taken on an Infralum FT-02 Fourier spectrometer for KBr tablets. Mass spectra were recorded on an MX 1321 instrument (70 eV electron ionization energy) for compound **7** and the remainder on an Agilent 6890N chromatograph with mass selective detector (equipped with a 30 m Agilent 19091S-433 HP-5MS capillary column of internal diameter 0.25 mm, 5% phenylmethylsiloxane, temperature program to 325ºC, and helium gas carrier (1 ml/min)).

TLC was carried out on Silufol UV-254 plates in the system hexane - diethyl ether (1:1) and revealed using iodine vapor or UV light. A DRT-400 mercury lamp was used for the photochemical reactions.

Photochemical Reaction of Styrene with Methanesulfobromide. Freshly distilled styrene (1.9 g, 18 mmol) and $MeSO_2Br$ [11], (2.86 g, 18 mmol) in anhydrous CH_2Cl_2 (15 ml) were placed in a quartz test tube. The reaction mixture was irradiated with UV light for 10 h at 20ºC. Solvent was removed *in vacuo* and the solid compound was purified by crystallization to give the sulfone **4b** (2.6 g).

Dehydrobromination Reaction of Compound 4b. A solution of Na_2CO_3 (9.1 g, 86 mmol) in water (50 ml) was added to a solution of compound **4b** (17.1 g, 65 mmol) in dioxane (50 ml), stirred for 20 h at 20ºC, and then diluted with water (150 ml). The finely crystalline solid was filtered off, washed with water (100 ml), and dried in air to give compound **1b** (10.2 g). Its ^{1}H and ^{13}C NMR spectra were identical to those given in [2].

Bromination of Compound 1b. A solution of bromine (3.52 g, 22 mmol) in anhydrous CH_2Cl_2 (4 ml) was added with stirring to a solution of compound **1b** (4.0 g, 22 mmol) in CH_2Cl_2 (30 ml). Stirring was continued for 30 h at 20ºC. Removal of solvent *in vacuo* gave the semicrystalline material **5b** (4.14 g) as a 2.4:1 mixture of the *erythro* and *threo* diastereomers (from their ^{1}H NMR spectra) with an admixture of the starting sulfone **1b**. The minor (*threo* isomer) component was separated by crystallization. The main (*erythro* isomer) was separated as an oil with a stereochemical purity of 85%.

Dehydrobromination of the Dibromosulfone 5b. A solution of Na_2CO_3 (1.27 g, 12 mmol) in water (15 ml) was added to a solution of the mixture of compound **5b** diastereomers (3.42 g, 10 mmol) in dioxane (15 ml), stirred for 20 h at 20ºC, and then diluted with water (100 ml). The finely crystalline precipitate was filtered off, washed with water (50 ml), and dried in air to give the sulfone **2b** (2.1 g).

Hydrodebromination of Compound 2b. Zinc dust (0.15 g, 2.3 mmol) was added to a solution of compound **2b** (1.15 g, 4.4 mmol) in 1:1 aqueous acetic acid (2 ml). The reaction mixture was refluxed with stirring for 50 min, zinc dust was again added (0.16 g, 2.5 mmol), and stirring was continued under the same conditions for a further 1 h. The cooled reaction mixture was diluted with water (80 ml) and extracted with $CHCl_3$ (3×20 ml). The extract was dried over $MgSO_4$ and the solvent was removed *in vacuo*. Crystallization gave the sulfone **1b** (0.36 g, 45%).

Photochemical Reaction of Phenylacetylene with Methanesulfobromide. Freshly distilled phenylacetylene (2.0 g, 20 mmol) and $MeSO_2Br$ (3.2 g, 20 mmol) were dissolved in anhydrous CH_2Cl_2 (10 ml) in a quartz test tube. The tube was tightly covered and irradiated with UV light for 26 h at 20ºC. After distillation of solvent the semicrystalline residue was washed with ether (10 ml) to give the bromosulfone **3b** (1.83 g) with mp 66-67ºC (from a mixture of chloroform and CCl_4). Mp reported in [6] was 60-61ºC (ethanol).

Reaction of Compound 1a with CH-Acids (General Method). A suspension of NaH (60%, 0.17 g, 4.2 mmol) in mineral oil was washed with dry hexane. Solvent was removed by decantation and the remainder *in vacuo*. The vacuum was purged by the introduction of argon and was added of dry THF (5 ml). A solution of the CH- acid (3.8 mmol) in THF (10 ml) was added dropwise with stirring and cooling to 5ºC. The reaction mixture was stirred in the case of the malonic acid derivatives for 1 h at 20ºC and for the acetoacetic

derivatives for 3 h at 45ºC. A solution of the sulfone **1a** (3.8 mmol) in THF (10 ml) was added dropwise and the product was stirred for 20 h at 20ºC, diluted with water (250 ml), and neutralized with dilute (1:1) HCl. The precipitate was filtered off, washed with water, dried in air, and purified by crystallization.

Reaction of Compound 2a with Malononitrile. A solution of sodium malononitrile in THF (10 ml) was prepared from a 60% suspension of sodium hydride (0.23 g, 5.8 mmol) in mineral oil and malononitrile (0.18 g, 2.8 mmol). A solution of compound **2a** (0.84 g, 2.5 mmol) in THF (10 ml) was added and the mixture was stirred for 20 h at 20ºC after which it was diluted with water (250 ml), and neutralized with dilute (1:1) HCl. The precipitate was filtered off, washed with water, dried in air, and crystallized to give compound **7** (0.41 g).

Reaction of Acetylene 10b with Malononitrile. A solution of sodium malononitrile in THF (10 ml) was prepared from a 60% suspension of sodium hydride (0.15 g, 3.8 mmol) in mineral oil and malononitrile (0.22 g, 3.4 mmol). A solution of acetylene **10b** [6] (0.56 g, 3.1 mmol) in THF (10 ml) was added and the mixture was stirred for 18 h at 20ºC after which it was diluted with water (180 ml), neutralized with dilute (1:1) HCl and extracted with $CHCl_3$ (3×15 ml). The extracts were washed with water and dried over $MgSO_4$. Removal of solvent and crystallization gave compound **9b** (0.21 g, 28%).

Reaction of Compound 2b with Malononitrile. A solution of sodium malononitrile in THF (10 ml) was prepared from a 60% suspension of sodium hydride (0.25 g, 6.2 mmol) in mineral oil and malononitrile (0.22 g, 3.4 mmol). A solution of compound **2b** (0.8 g, 3.1 mmol) in THF (10 ml) was added and the mixture was stirred for 2.5 h after which it was diluted with water (200 ml), neutralized with dilute (1:1) HCl, extracted with $CHCl_3$, washed with water, and dried over $MgSO_4$. Evaporation of solvent *in vacuo* gave 0.45 g of a viscous oil which was recrystallized to give compound **9b** (0.27 g, 36%).

Reaction of Compounds 3a and 3b with Malononitrile (General Method). A solution of malononitrile (0.2 g, 3.0 mmol) in THF (10 ml) was added dropwise with stirring and cooling to 5ºC over 10 min under a dry argon atmosphere to a 60% suspension of NaH (0.25 g, 6.2 mmol) in mineral oil which had been washed and dried as reported above. Stirring was continued for 1 h at 20ºC. A solution of compound **3a** or **3b** (2.7 mmol) in THF (10 ml) was added and stirred at 20ºC for a further 20 h, diluted with water (200 ml), and neutralized using dilute (1:1) HCl. The precipitated ethylidene compound **9a** or **9b** was filtered off, washed with water, dried in air, and purified by crystallization.

Reaction of Compounds 2b and 3b with Sodium Methylate (General Method). Either compound **2b** or **3b** (0.31 g, 1.2 mmol) was added to a solution of sodium methylate prepared from metallic sodium (0.11 g, 4.8 mmol) and anhydrous methanol (5 ml). The mixture was refluxed for 30 min, neutralized using 1:1 HCl solution with thymol blue, diluted with water (30 ml), and extracted with CH_2Cl_2 (3×10 ml). The extract was washed with water and dried over $MgSO_4$. Solvent was removed *in vacuo*. Crystallization of the solid residue gave about 0.23 g of compound **11**.

Reaction of sulfone 2b with KOH. The sulfone **2b** (1.15 g, 4.4 mmol) was added to a solution of KOH (0.24 g, 4.4 mmol) in a mixture of methanol (15 ml) and water (5 ml). The product was stirred for 5 h at 20ºC, diluted with water (20 ml), and extracted with $CHCl_3$ (3×10 ml). The extracts were washed with water and dried over $MgSO_4$ to give the ketone **12** (0.61 g) with mp 105-106ºC (a mixture of chloroform and CCl_4). The melting point is given as 106-107ºC in [12].

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