Bis(sulfonyl)methyl Insertion into Alkenyl versus Phenyl Carbon−Hydrogen Bonds in the Reaction of Bis(sulfonyl)iodonium Ylides with Highly Phenylated Ethylenes

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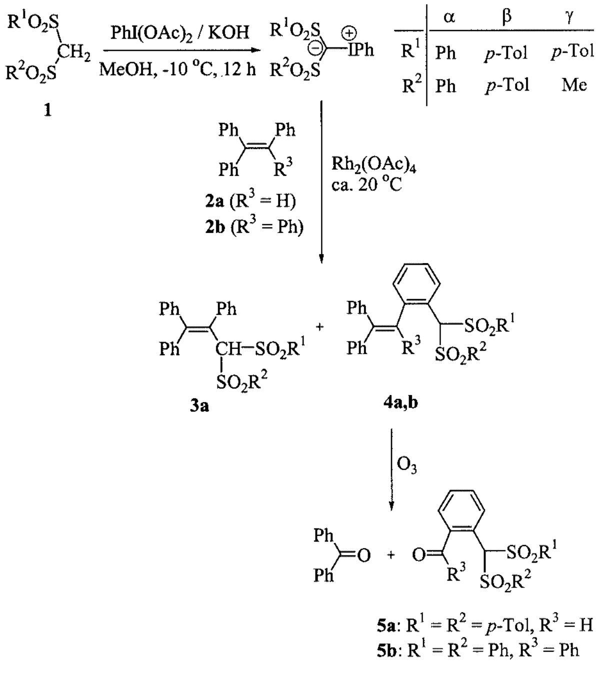
The reaction of bis(sulfonyl)iodonium ylides **α**–**γ** with triphenylethylene (**2a**) and tetraphenylethylene (**2b**) affords insertion products into the alkenyl and phenyl carbon–hydrogen bonds of the substrate. A mechanistically perplexing feature is the diversity displayed in the reactivity pattern of the bis(sulfonyl)iodonium ylides in their reaction with the phenylated alkenes.

Introduction

Although iodonium ylides,[1] a versatile class of hypervalent iodine compounds,[2] are structurally quite distinct from the corresponding diazo compounds, they are similar to them in their reactivity towards alkenes. Thus, the photochemical and thermal Cu(acac)$_2$-catalyzed reactions of bis(sulfonyl)iodonium ylides with alkenes afford cyclopropanes,[3] presumably through carbene intermediates, analogous to the related bis(sulfonyl)diazomethanes.[3d] In contrast, the thermal Rh$_2$(OAc)$_4$-catalyzed reaction[3a,3c,4] of these iodonium ylides with phenylated alkenes − for example, stilbenes − leads stereoselectively to *trans*,*trans*-configured 1,2,3-trisubstituted indanes. In view of the synthetic value of this unusual process, the incentive of the present study was to extend this novel cycloaddition reaction to other phenylated alkenes. Unexpectedly, the reaction of bis(sulfonyl)iodonium ylides **α**−**γ** with triphenylethylene (**2a**) and tetraphenylethylene (**2b**) gave insertion products into the alkenyl and phenyl carbon−hydrogen bonds of the substrates. What is unusual about this insertion reaction is that carbene chemistry appears not to be involved.

Results and Discussion

The disulfonyliodonium ylides **α**−**γ** were prepared readily[3a] from the corresponding disulfones **1** by treatment with diacetoxyiodobenzene and KOH as base at −10 °C (Scheme 1). These labile ylides may be stored at −30 °C for several weeks without decomposition, and since they are practically insoluble in common organic solvents (except DMSO), the reaction of the ylides with the alkenes **2** has been conducted under heterogeneous conditions. All reactions were run until complete consumption of the ylide occurred, which was indicated by the change from a heterogeneous mixture to a clear solution. The reactions with triphenylethylene (**2a**) were carried out in acetonitrile, whereas dichloromethane had to be used for tetraphenylethylene (**2b**) because it is insoluble in acetonitrile. The mixtures of



Scheme 1

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Table 1. Reactions of iodonium ylides **α**−**γ** with alkenes **2**

Entry[a]	Ylide			Alkene		Time[b]	Conv.[c]	PB[d]	Yield (%)			
		R^1	R^2		R^3	(h)	(%)	(%)	**3a**		**4**	
									Abs.[e]	Rel.[f]	Abs.[e]	Rel.[f]
1	**α**	Ph	Ph	**2a**	H	18	22	87	35	58	23	32
2	**β**	*p*Tol	*p*Tol	**2a**	H	56	24	89	36	67	27[g]	34[g]
3	**γ**	*p*Tol	Me	**2a**	H	8.5	29	91	39	50	28	36
4	**α**	Ph	Ph	**2b**	Ph	1.5	16	80	–	–	31	73
5	**β**	*p*Tol	*p*Tol	**2b**	Ph	0.2	13	82	–	–	26	74
6	**γ**	*p*Tol	Me	**2b**	Ph	0.2	18	92	–	–	29	84

[a] All reactions were carried out by stirring a suspension of ylides **α**−**γ** (1 equiv.) and alkene **2** (2.8 equiv.), in acetonitrile for **2a** and in dichloromethane for **2b**, in the presence of a catalytic amount of $Rh_2(OAc)_4$. [b] Time required for complete consumption of the ylide. [c] Conversion of the alkene **2**, as determined after isolation by silica gel chromatography; the conversion of the ylide was > 95% in all cases. [d] Product balance; The sum of yields of all isolated products. The remaining yield, not shown in the Table, reflects the percentage of β-disulfone **1**. [e] Yield of isolated product (relative to 100% consumption of the ylide) after silica gel chromatography. [f] Normalized to 100% conversion of the alkene. [g] Determined by ^1H NMR spectroscopy, error ±5% of the stated value.

products were separated by flash chromatography on silica gel. The results of the reactions are summarized in Table 1.

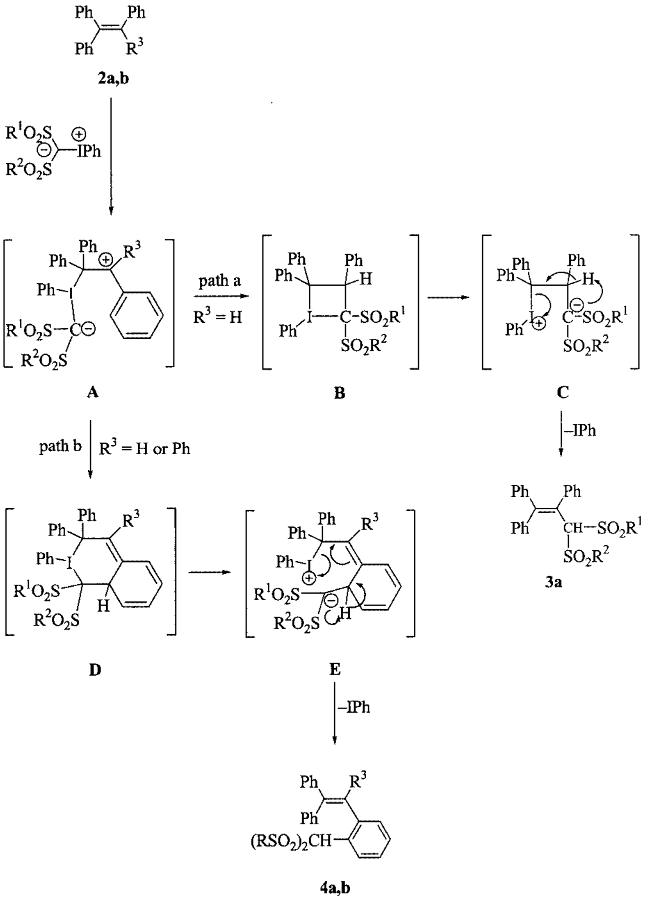
The adducts **3a** and **4a** were produced from the ylides **α**−**γ** and triphenylethylene (**2a**) in moderate yields (Entries 1−3), which are referred to the conversion of triphenylethylene. The reaction of the ylides **α**−**γ** with tetraphenylethylene (**2b**) gave only the adducts **4b** in moderate yields (Entries 4−6), based on the conversion of tetraphenylethylene.

All reactions of the ylides **α**−**γ** with the alkenes **2** were carried out in the presence of catalytic amounts of $Rh_2(OAc)_4$; much longer reaction times were necessary in the absence of the catalyst, but the same product compositions were obtained.[3c] The adducts **3** and **4** were isolated in moderate yields (up to 67%, relative to the ylide) by flash chromatography on silica gel, and the remainder of the ylides were converted into the corresponding β-disulfones **1**. It should be emphasized that, in relation to the amount of olefin consumed, high yields (up to 95%) of the adducts **3** and **4** are registered (Table 1). These yields indicate that efficient and clean processes operate, except that substantial amounts (up to 74%) of the ylides are diverted to β-disulfones through decomposition. It is worth mentioning that traces (ca. 3%) of benzaldehyde and benzophenone were also isolated from the reactions of triphenylethylene and tetraphenylethylene, respectively, together with the disulfones **1**.

The adducts **3a** and **4a** were characterized by NMR (H,H-COSY, C,H-COSY, DEPT), IR, and mass spectra. In the case of the adduct **3aγ** for example, the two pairs of IR absorption bands at 1325/1315 and 1170/1155 cm^{-1} correspond to the sulfonyl groups. The ^1H NMR spectrum displays the signal of the proton attached to the carbon atom bearing the methylsulfonyl and *p*-toluenesulfonyl groups as a singlet at $\delta = 5.98$ ppm, which is CH-correlated with the peak at $\delta = 88.5$ ppm in the ^{13}C NMR spectrum. In the case of the adducts **4a** and **4b** − for example, **4aγ** − the signal of the proton attached to the carbon atom that bears the methylsulfonyl and *p*-toluenesulfonyl groups appears as a singlet at $\delta = 5.21$ ppm in the ^1H NMR spectrum, and is CH-correlated with the peak at $\delta = 87.2$ ppm in the ^{13}C NMR spectrum. Similarly, the ^1H NMR spectrum of the adduct **4bα** shows also a singlet, at $\delta = 5.34$ ppm, for the methine unit bearing the benzenesulfonyl groups, which correlates with the peak at $\delta = 88.3$ ppm in the ^{13}C NMR spectrum. Also, the molecular ion peak ($m/z = 626$) was observed in the mass spectrum. Furthermore, ozonolysis of the adducts **4aβ** and **4bα** afforded benzophenone and the aldehyde **5a** and ketone **5b** (Scheme 1), respectively, which establishes the assigned structures unequivocally.

In regard to the mechanism for the formation of the adducts **3a** and **4a**,**b**, such carbon−hydrogen insertions are characteristic of carbene reactions. Nonetheless, although carbene insertion products have been observed in the photochemical and metal-catalyzed transformations of iodonium ylides,[5] the involvement of carbenes (or carbenoids) in such reactions has been questioned.[6] In the present case of the insertion products **3a** and **4a**,**b**, it is unlikely that ylides **α**−**γ** generate bis(sulfonyl)carbenes under the mild (Rh^{II}-catalyzed) reaction conditions, in contrast to carbenes reported for their $Cu(acac)_2$-catalyzed thermal decompositions or in their photolyses.[3b] Had a carbene intervened in the present case − as has been suggested for the $Cu(acac)_2$-catalyzed thermal reaction of ylide **α** with triphenylethylene − the phenyl benzenethiosulfonate ($PhSO_2SPh$) would likely have been detected, since it is the typical product derived from the bis(phenylsulfonyl)carbene.[3a,3d]

In view of these facts, we propose the mechanism in Scheme 2, which is consistent with the results presented herein. First, the iodonium functionality of the ylide attacks the alkene **2** electrophically[6a] to generate the dipolar species **A**; subsequent ring closure (path a) leads to the four-membered cyclic trivalent iodine compound **B**. Although such iodine species have been proposed previously[6b] to undergo elimination of iodobenzene and produce the corresponding cyclopropanes, instead we suggest that ring opening occurs to give the dipolar intermediate **C**. Elimination of iodobenzene,[7] followed by hydrogen atom migration, leads to the adduct **3a**. Alternatively, we suggest that the



Scheme 2

bis(sulfonyl)-centered carbanion of the dipolar entity **A** attacks the phenyl rings of the alkenes **2a**,**b** nucleophilically to give the bicyclic trivalent iodine compounds **D** (path b). Ring opening of the latter to the dipolar structure **E**, followed by elimination of iodobenzene[7] and aromatization, affords the bis(sulfonyl)methyl insertion products **4a**,**b**. That about twice as much **3a** (alkene insertion) is formed relative to **4a** (phenyl insertion) in the reaction of triphenylethylene (**2a**) (Table 1, cf. rel. yields) is to be expected, since the generation of the intermediate **B** involves merely bond formation through charge collapse, whereas intermediate **D** requires dearomatization.

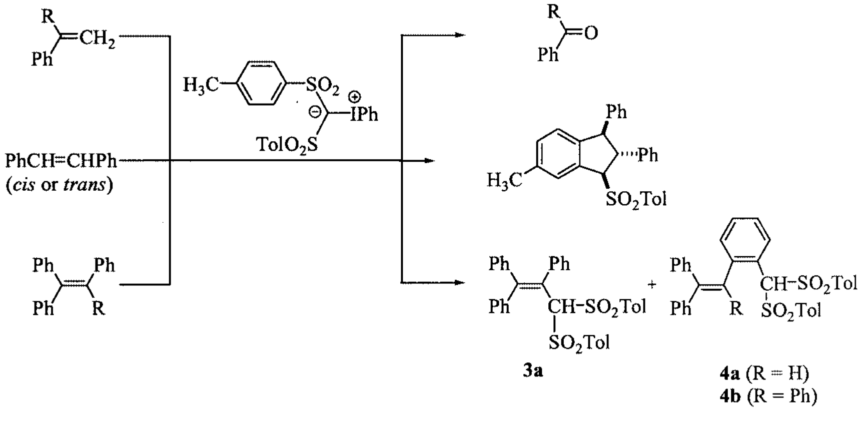
A mechanistically perplexing feature is the diversity displayed in the reactivity pattern of the bis(sulfonyl)iodonium ylides in their reaction with the phenylated ethylenes, as shown in Scheme 3.

Styrene and 1,1-diphenylethylene afford, by oxidation, the cleavage products benzaldehyde and benzophenone,[3a,3b] respectively, yet the *trans*,*trans*-configured 1,2,3-trisubstituted indanes are formed stereoselectively from stilbenes[4] and triphenylethylene and tetraphenylethylene lead to the insertion products **3** and **4**. This trichotomy in reaction types is unprecedented for the phenylated ethylenes and reveals the temperamental chemical behavior of the iodonium ylides, namely to engage in either oxidative cleavage, cycloaddition, or insertion, depending upon the extent and pattern of phenylation of the ethylene substrate.

Experimental Section

General Aspects: ^1H and ^{13}C NMR spectra were recorded with a Bruker AC 200 (^1H: 200 MHz; ^{13}C: 50 MHz) or a Bruker Avance 400 (^1H: 400 MHz; ^{13}C: 100 MHz) spectrometer. For the IR spectra, a Perkin−Elmer 1420 ratio-recording infrared spectrophotometer was used. TLC analysis was conducted on precoated silica gel foils 60 F_{254} (20 × 20 cm) from Merck, Darmstadt, Germany. The spots were visualized either by UV irradiation (254 nm) or with a 5% polymolybdic acid solution in ethanol. Silica gel (32−62 nm) from Woelm, Erlangen, Germany, was used for column chromatography. Melting points (uncorrected) were determined with a Büchi B-545 apparatus. Elemental analyses were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg. Mass spectra were carried out with a Finnigan MAT8200; the exact mass was determined with a Finnigan MAT90. All commercial reagents were used without further purification. Solvents were dried by standard methods and purified by distillation before use. Ylides $\alpha-\gamma$ were synthesized according to literature procedures.[3a]

General Procedure for the Reaction of Ylides $\alpha-\gamma$ with the Alkenes 2: A catalytic amount (0.1−0.2 mol %) of $Rh_2(OAc)_4$ was added to a suspension of the particular ylide (0.56−1.00 equiv.) and alkene (1.50−2.70 equiv.) in acetonitrile or in dichloromethane (10 mL)



Scheme 3

and the mixture was stirred at room temp. (ca. 20 °C) until a clear solution was produced (complete consumption of the ylide). The solvent was removed (20 °C at 10 Torr) and the residue was chromatographed on silica gel with a mixture of CH_2Cl_2 and petroleum ether as eluent. Iodobenzene eluted first, followed by the adducts **3a**, **4**, and disulfones **1**.

Reaction of Ylide α with Triphenylethylene (2a): A suspension of ylide **α** (288 mg, 0.58 mmol) and triphenylethylene (400 mg, 1.56 mmol) in acetonitrile (10 mL) was stirred for 18 h according to the general procedure above. The solvent was evaporated (20 °C at 10 Torr) and the residue was chromatographed on silica gel (CH_2Cl_2/petroleum ether, 1:4) to yield **3aα** (110 mg, 35%) and **4aα** (73.0 mg, 23%) at an olefin conversion of 22%.

1-[Bis(phenylsulfonyl)methyl]triphenylethylene (3aα): Colorless plates, m.p. 206−207 °C. IR (KBr): $\tilde{\nu}$ = 3070, 2920, 1495, 1450, 1330, 1325, 1315, 1225, 1200, 1170, 1155, 1135, 1080, 1035, 1000 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.39 (s, 1 H, CH), 6.93−7.10 (m, 8 H, aromatic), 7.21−7.32 (m, 7 H, aromatic), 7.35−7.52 (m, 10 H, aromatic) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 88.7 (d), 126.0 (s), 127.5 (d), 127.9 (d), 128.4 (d), 128.8 (d), 129.3 (d), 129.5 (d), 130.8 (d), 132.2 (d), 134.4 (d), 136.0 (s), 139.9 (s), 141.8 (s), 141.9 (s), 155.4 (s) ppm. $C_{33}H_{26}O_4S_2$ (550.7): calcd. C 71.98, H 4.76, S 11.64; found C 71.59, H 4.93, S 11.91.

1-[Bis(phenylsulfonyl)methyl]-2-(2,2-diphenylvinyl)benzene (4aα): Colorless powder, m.p. 136−137 °C. IR (KBr): $\tilde{\nu}$ = 3090, 2950, 1600, 1505, 1455, 1340, 1320, 1165, 1155, 1085, 1025, 1005, 855 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.33 (s, 1 H, CH), 6.88 (s, 1 H, CH), 6.97 (d, *J* = 6.9 Hz, 1 H, aromatic), 7.12−7.14 (m, 4 H, aromatic), 7.26−7.34 (m, 7 H, aromatic), 7.42−7.53 (m, 8 H, aromatic), 7.58−7.66 (m, 4 H, aromatic) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.3 (d), 123.4 (s), 126.7 (d), 127.6 (d), 127.7 (d), 128.2 (d), 128.6 (d), 128.8 (d), 129.6 (d), 129.7 (d), 129.8 (d), 130.2 (d), 134.4 (d), 137.9 (s), 139.6 (s), 142.8 (s), 144.5 (s) ppm. HR-MS (EI): $C_{33}H_{26}O_4S_2$ $[M^+]$: calcd. 550.1272; found 550.1265.

Reaction of Ylide β with Triphenylethylene (2a): A suspension of ylide **β** (380 mg, 0.72 mmol) and triphenylethylene (500 mg, 1.95 mmol) in acetonitrile (10 mL) was stirred for 56 h according to the general procedure above. The solvent was evaporated (20 °C at 10 Torr) and the residue was chromatographed on silica gel (CH_2Cl_2/petroleum ether, 1:4) to yield **3aβ** (152 mg, 36%) and a 1:1 mixture (236 mg) of **4aβ** and **1β**, at an olefin conversion of 24%.

1-[Bis(*p*-toluenesulfonyl)methyl]triphenylethylene (3aβ): Colorless needles, m.p. 225−226 °C. IR (KBr): $\tilde{\nu}$ = 2910, 1595, 1490, 1445, 1335, 1315, 1300, 1290, 1205, 1185, 1150, 1130, 1075, 1035, 1015, 850, 815 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 6 H, $2CH_3$), 6.33 (s, 1 H, CH), 6.94−7.00 (m, 2 H, aromatic), 7.01−7.11 (m, 10 H, aromatic), 7.24 (d, *J* = 8.5 Hz, 4 H, aromatic), 7.31−7.33 (m, 2 H, aromatic), 7.39−7.46 (m, 5 H, aromatic) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (q), 88.6 (d), 126.0 (s), 127.1 (d), 127.4 (d), 127.6 (d), 127.7 (d), 128.0 (d), 129.0 (d), 129.1 (d), 129.2 (d), 129.3 (d), 130.5 (d), 132.0 (d), 135.8 (s), 136.7 (s), 141.6 (s), 141.7 (s), 144.7 (s), 154.6 (s) ppm. $C_{35}H_{30}O_4S_2$ (578.7): calcd. C 72.64, H 5.22, S 11.08; found C 72.56, H 5.47, S 10.92.

1-[Bis(*p*-toluenesulfonyl)methyl]-2-(2,2-diphenylvinyl)benzene (4aβ): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 6 H, $2CH_3$), 5.33 (s, 1 H, CH), 6.88 (d, *J* = 8.1 Hz, 1 H, aromatic), 6.90 (s, 1 H, aromatic), 7.12−7.16 (m, 4 H, aromatic), 7.22 (d, *J* = 8.0 Hz, 4 H, aromatic), 7.30−7.34 (m, 7 H), 7.60 (d, *J* = 8.3 Hz, 4 H, aromatic), 7.65−7.68 (m, 2 H, aromatic) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7 (q), 88.2 (d), 123.7 (s), 126.8 (d), 127.5 (d), 127.8 (d), 127.9 (d), 128.2 (d), 128.6 (d), 129.3 (d), 129.5 (d), 129.6 (d), 130.1 (d), 135.0 (s), 139.7 (s), 142.8 (s), 144.2 (s), 145.5 (s) ppm.

Reaction of Ylide γ with Triphenylethylene (2a): A suspension of ylide **γ** (450 mg, 1.0 mmol) and triphenylethylene (690 mg, 2.7 mmol) in acetonitrile (10 mL) was stirred for 8.5 h according to the general procedure above. The solvent was evaporated (20 °C at 10 Torr) and the residue was chromatographed on silica gel (CH_2Cl_2/petroleum ether, 1:1) to yield **3aγ** (195 mg, 39%) and **4aγ** (141 mg, 28%), at an olefin conversion of 29%.

1-[(Methylsulfonyl)(*p*-toluenesulfonyl)methyl]triphenylethylene (3aγ): Colorless cubes, m.p. 212−213 °C. IR (KBr): $\tilde{\nu}$ = 1520, 1465, 1350, 1335, 1180, 1160, 1135, 1095, 1040, 980, 825 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 6 H, CH_3), 2.39 (d, *J* = 0.8 Hz, 3 H, CH_3), 5.98 (d, *J* = 0.8 Hz, 1 H, CH), 7.06 (s, 5 H, aromatic), 7.11−7.13 (m, 2 H, aromatic), 7.23−7.29 (m, 6 H, aromatic), 7.43−7.47 (m, 4 H, aromatic), 7.59 (d, *J* = 6.7 Hz, 2 H, aromatic) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (q), 41.6 (q), 88.5 (d), 125.5 (s), 127.1 (d), 127.3 (d), 127.6 (d), 128.1 (d), 128.4 (d), 128.9 (d), 129.2 (d), 129.4 (d), 130.0 (d), 130.1 (d), 131.7 (d), 135.9 (s), 137.3 (s), 140.7 (s), 140.8 (s), 145.2 (s), 159.3 (s) ppm. HRMS (EI): $C_{29}H_{26}O_4S_2$ $[M^+]$: calcd. 502.1272; found 502.1272.

2-(2,2-Diphenylvinyl)-1-[(methylsulfonyl)(*p*-toluenesulfonyl)methyl]benzene (4aγ): Colorless powder, m.p. 147−148 °C. IR (KBr): $\tilde{\nu}$ = 3070, 3040, 2940, 1600, 1515, 1500, 1450, 1420, 1325, 1160, 1145, 1090, 1035, 1025, 975, 895, 855, 845, 820 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 3.33 (s, 3 H, CH_3), 5.19 (s, 1 H, CH), 6.92 (s, 1 H, CH), 6.96 (d, *J* = 8.3 Hz, 2 H, aromatic), 7.10 (d, *J* = 8.3 Hz, 2 H, aromatic), 7.18−7.18 (m, 2 H, aromatic), 7.23 (d, *J* = 8.1 Hz, 2 H, aromatic), 7.29−7.35 (m, 8 H, aromatic), 7.50 (d, *J* = 8.3 Hz, 2 H, aromatic) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8 (q), 43.1 (q), 87.3 (d), 122.7 (s), 126.7 (d), 127.6 (d), 127.8 (d), 127.9 (d), 128.3 (d), 128.7 (d), 129.3 (d), 129.8 (d), 130.2 (d), 130.7 (d), 133.3 (s), 139.8 (s), 142.8 (s), 144.6 (s), 146.0 (s) ppm. HRMS (EI): $C_{29}H_{26}O_4S_2$ $[M^+]$: calcd. 502.1272; found 502.1272.

Reaction of Ylide α with Tetraphenylethylene (2b): A suspension of ylide **α** (278 mg, 0.56 mmol) and tetraphenylethylene (500 mg, 1.5 mmol) in dichloromethane (10 mL) was stirred for 1.5 h according to the general procedure above. The solvent was evaporated (20 °C at 10 Torr) and the residue was chromatographed on silica gel (CH_2Cl_2/petroleum ether, 1:4) to yield of **4bα** (110 mg, 31%), at an olefin conversion of 16%.

1-[Bis(phenylsulfonyl)methyl]-2-(triphenylvinyl)benzene (4bα): Colorless plates, m.p. 252−253 °C. IR (KBr): $\tilde{\nu}$ = 3040, 3000, 2980, 1480, 1435, 1320, 1315, 1305, 1190, 1160, 1150, 1125, 1070, 1020, 995, 865 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.34 (s, 1 H, CH), 6.87−7.03 (m, 9 H, aromatic), 7.08−7.19 (m, 10 H, aromatic), 7.41−7.49 (m, 4 H, aromatic), 7.60−7.73 (m, 6 H, aromatic) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 88.3 (d), 123.7 (s), 127.0 (d), 127.2 (d), 128.0 (d), 129.0 (d), 130.1 (d), 131.5 (d), 131.6 (d), 131.9 (d), 134.8 (d), 138.1 (s), 139.9 (s), 142.5 (s), 143.3 (s), 143.5 (s), 143.6 (s), 146.6 (s) ppm. HRMS (EI): $C_{39}H_{30}O_4S_2$ $[M^+]$: calcd. 626.1585; found 626.1580.

Reaction of Ylide β with Tetraphenylethylene (2b): A suspension of ylide **β** (400 mg, 0.76 mmol) and tetraphenylethylene (680 mg, 2.05 mmol) in dichloromethane (10 mL) was stirred for 10 min according to the general procedure above. The solvent was evaporated (20 °C at 10 Torr) and the residue was chromatographed on silica gel (CH_2Cl_2/petroleum ether, 1:4) to yield of **4bβ** (130 mg, 26%), at an olefin conversion of 13%.

1-[Bis(*p*-toluenesulfonyl)methyl]-2-(triphenylvinyl)benzene (4bα): Colorless powder, m.p. 267−268 °C. IR (KBr): $\tilde{\nu}$ = 1600, 1500, 1450, 1340, 1155, 1085, 870, 820 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.43 (s, 6 H, 2CH$_3$), 5.29 (s, 1 H, CH), 6.89−6.93 (m, 4 H, aromatic), 6.98−7.03 (m, 5 H, aromatic), 7.07−7.19 (m, 10 H, aromatic), 7.23 (d, *J* = 8.0 Hz, 4 H, aromatic), 7.59 (d, *J* = 8.3 Hz, 4 H, aromatic) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.7 (q), 88.4 (d), 123.8 (s), 126.6 (d), 126.7 (d), 126.8 (d), 127.6 (d), 127.7 (d), 129.3 (d), 129.8 (d), 131.1 (d), 131.2 (d), 131.3 (d), 131.4 (d), 134.9 (s), 139.6 (s), 142.0 (s), 143.0 (s), 143.2 (s), 143.3 (s), 145.5 (s), 146.0 (s) ppm. HRMS (EI): $C_{41}H_{34}O_4S_2$ [M$^+$]: calcd. 654.1898; found 654.1896.

Reaction of Ylide γ with Tetraphenylethylene (2b): A suspension of ylide **γ** (350 mg, 0.78 mmol) and tetraphenylethylene (500 mg, 1.5 mmol) in dichloromethane (10 mL) was stirred for 10 min according to the general procedure above. The solvent was evaporated (20 °C at 10 Torr) and the residue was chromatographed on silica gel (CH$_2$Cl$_2$/petroleum ether, 1:1) to yield of **4bγ** (132 mg, 29%), at an olefin conversion of 18%.

1-[(Methylsulfonyl)(*p*-toluenesulfonyl)methyl]-2-(triphenylvinyl)benzene (4bγ): Colorless cubes, m.p. 281−282 °C. IR (KBr): $\tilde{\nu}$ = 2920, 1590, 1490, 1440, 1410, 1320, 1145, 1080, 1025, 1015, 970, 860, 815 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.43 (s, 3 H, CH$_3$), 3.30 (s, 3 H, CH$_3$), 5.21 (s, 1 H, CH), 6.96−7.04 (m, 8 H, aromatic), 7.06 (d, *J* = 8.2 Hz, 2 H), 7.09−7.17 (m, 9 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 7.46 (d, *J* = 8.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.8 (q), 43.2 (q), 87.3 (d), 122.7 (s), 126.7 (d), 126.9 (d), 127.6 (d), 127.7 (d), 127.8 (d), 129.3 (d), 130.3 (d), 130.6 (d), 131.2 (d), 131.3 (d), 131.7 (d), 133.0 (s), 139.7 (s), 142.2 (s), 142.9 (s), 143.2 (s), 143.3 (s), 146.0 (s), 146.3 (s) ppm. HRMS (EI): $C_{35}H_{30}O_4S_2$ [M$^+$]: calcd. 578.1585; found 578.1581.

General Procedure for the Ozonolysis: A gentle stream of ozone gas was passed through a solution of the particular alkene in dichloromethane (5 mL) and methanol (drops) at −78 °C for 3 h. After warming up to room temp. (ca. 20 °C), dimethyl sulfide (0.2 mL) was added and the resulting mixture was stirred at room temp. (ca. 20 °C) for 18 h. After removal of the solvent (30 °C at 10 Torr), the residue was dissolved in dichloromethane (30 mL) and extracted with brine (2 × 30 mL). The organic phase was dried with MgSO$_4$ and after removal of the solvent (20 °C at 10 Torr), the crude product was chromatographed on silica gel with a mixture of CH$_2$Cl$_2$ and petroleum ether as eluent. Benzophenone eluted first, followed by the aldehyde **5a** and the ketone **5b**.

Ozonolysis of the Mixture of 1-[Bis(*p*-toluenesulfonyl)methyl]-2-(2,2-diphenylvinyl)benzene (4aβ) and the Bis(*p*-toluenesulfonyl)methane (1β): A solution of the 1:1 mixture (236 mg) of **4aβ** and **1β** was ozonolyzed according the general procedure above. The resulting residue was chromatographed on silica gel (CH$_2$Cl$_2$/petroleum ether, 1:1) to yield aldehyde **5a** (69.0 mg, 76%) as a colorless powder, m.p. 82−83 °C. IR (KBr): $\tilde{\nu}$ = 2940, 1670, 1605, 1345, 1310, 1285, 1160, 1085, 1020, 945, 935, 875, 820 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.42 (s, 3 H, CH$_3$), 2.43 (s, 3 H, CH$_3$), 5.49 (s, 1 H, CH), 7.24−7.28 (m, 5 H, aromatic), 7.49 (t, *J* = 7.7 Hz, 1 H, aromatic), 7.60−7.68 (m, 5 H, aromatic), 7.75−7.79 (m, 1 H, aromatic), 10.01 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.7 (q), 88.2 (d), 128.4 (d), 129.6 (d), 129.7 (d), 129.8 (d), 129.9 (d), 130.1 (d), 134.8 (s), 136.9 (s), 138.9 (s), 146.1 (s), 191.4 (d) ppm. HRMS (EI): $C_{22}H_{20}O_5S_2$ [M$^+$]: calcd. 428.0752; found 428.0755.

Ozonolysis of 1-[Bis(phenylsulfonyl)methyl]-2-(triphenylvinyl)benzene (4bα): A solution of **4bα** (30.0 mg, 48 μmol) was ozonolyzed according the general procedure above. The resulting residue was chromatographed on silica gel (CH$_2$Cl$_2$/petroleum ether, 1:1) to yield ketone **5b** (16.0 mg, 70%) as colorless plates, m.p. 139−140 °C. IR (KBr): $\tilde{\nu}$ = 2995, 1680, 1485, 1355, 1335, 1320, 1305, 1195, 1165, 1095, 965, 950, 895 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 5.53 (s, 1 H, CH), 7.45−7.53 (m, 7 H, aromatic), 7.58−7.74 (m, 7 H, aromatic), 7.75−7.83 (m, 5 H, aromatic) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 88.1 (d), 128.8 (d), 129.3 (d), 130.0 (d), 130.4 (d), 133.3 (d), 135.2 (s), 137.2 (s), 138.0 (s), 139.4 (s), 196.4 (s) ppm. HRMS (EI): $C_{26}H_{20}O_5S_2$ [M$^+$]: calcd. 476.0752; found 476.0746.

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