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DONOR SUBSTITUTED SULFONYL CARBENES - 1. METHOXY ARYLSULFONYL CARBENES

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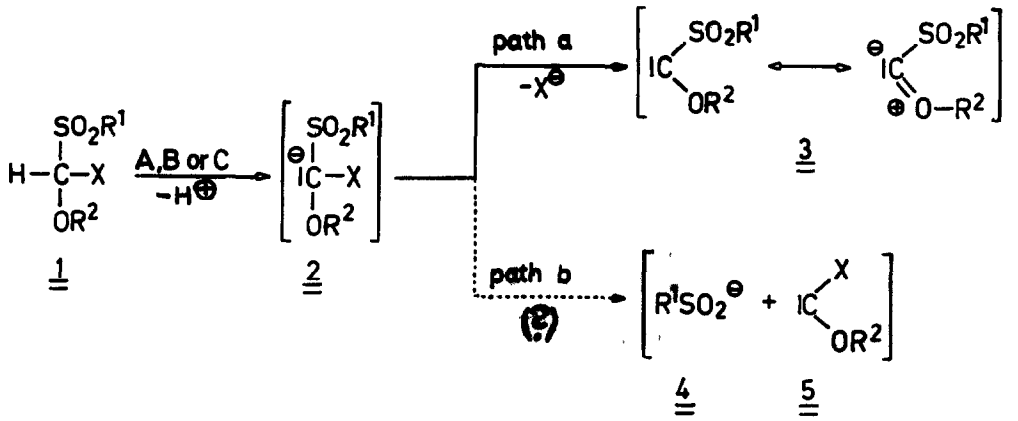
Abstract: Alkoxy arylsulfonyl carbenes 3 are generated by α elimination of hydrogen halide from (alkoxy)(halogeno)methyl aryl sulfones 1. Their self-decomposition as well as trapping reactions with diazoalkanes and with appropriate olefins are described. The structures of obtained cyclopropanes 21 and 23 are elucidated by ^{1}H NMR methods.

α-Elimination of hydrogen chloride from chloromethyl aryl sulfones via α-chloro-α-sulfonyl carbanions has been described to be unsuccessful[1] with respect to carbene generation. Eliminations of halide anion from these anions are known only after preceding additions to polar double bonds and subsequent intramolecular nucleophilic displacements[2]. However, formation of a carbene becomes possible if the strong electron withdrawing effect of the sulfonyl substituent is compensated by an electron donating substituent as the methoxy group at the same carbon atom[3]. In the absence of special trapping reagents the disulfones 11 are obtained as main products in consequence of S addition of ambident sulfinate 4 to carbene 3[4] (cf. scheme 3) in analogy to sulfinate addition to methoxy methoxycarbonyl carbene[5]. This assumption is proved by generation of carbene 3a in the presence of p-chlorobenzenesulfinate yielding the unsymmetrically substituted β-disulfone 11c. The origin of sulfinate 4 was supposed to stem from a competitive α-elimination (path b), however, trapping products of the known alkoxy halogeno carbenes (i.e. R^2 = Me, X = Cl)[6] could not be found though Moss[7] reported on path b with 1d (X = F).

Scheme 1: Generation of carbenes from 1

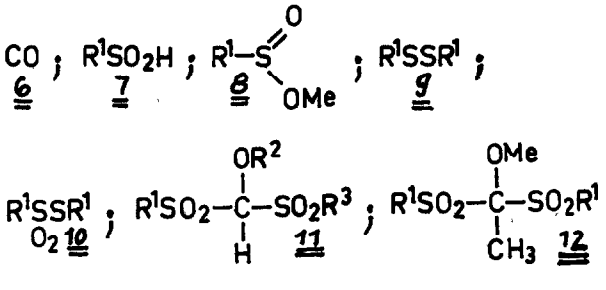


	R^1	R^2	X
1a	$4\text{-}CH_3C_6H_4$	CH_3	Cl
b	"	CH_3	Br
c	"	C_2H_5	Br
d	"	CH_3	F[7]

A: n-BuLi/THF/-78°C
B: KOt-Bu/THF (or DMF) } different
C: 50% KOH/PTC/H_2O-Et_2O } temperatures

In order to get more insight into this reaction and into the chemistry of carbenes 3, reaction conditions are varied, by-products are identified, and other nucleophilic trapping agents than sulfinate are applied. Deprotonation of 1 with n-BuLi (method A) or with potassium tert.-butylate in THF or DMF at -78°C (method B) as well as with KOH under phase-transfer conditions (PTC) at 0°C or at ambient temperature (method C) leads essentially to the same products:

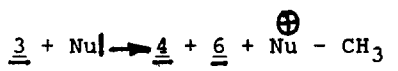
Scheme 2: Identified self-decomposition products of carbenes 3



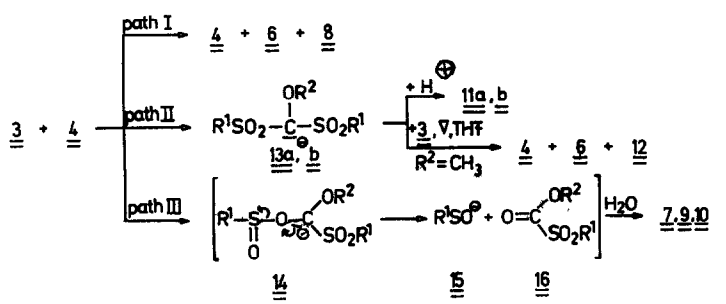
7-10,12 : R^1=4-$CH_3C_6H_4$
11a: R^1,R^3=4-$CH_3C_6H_4$; R^2=CH_3
11b: R^1,R^3=4-$CH_3C_6H_4$; R^2=C_2H_5
11c: R^1=4-$CH_3C_6H_4$; R^2=CH_3; R^3=4-ClC_6H_4

Formation of 12 takes place only at elevated temperature in THF obviously by methylation of anion 13 (scheme 4). Carbene 3 as ambident electrophile suffers a fragmentation catalyzed by any reactive nucleophile present in the reaction mixture yielding 4 (7) and 6; carbon monoxide (6) formation by decomposition of related alkoxy halocarbenes has already been described[6a,6d-i].

Scheme 3: Nucleophile catalyzed formation of sulfinate 4 from 3



Scheme 4: Sulfinate 4-catalyzed chain reactions

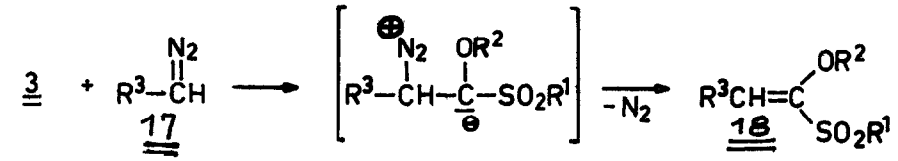


O-Additions of sulfinates to carbenes are known[8], and the resulting sulfinyloxy carbanions like 14 yield carbonyl compounds and sulfenate 15[9]. On the other hand, alkyl sulfonylformates 16 are cleaved very easily by nucleophiles yielding sulfinic acids[10] whereas 9 and 10 are known to be decomposition products of sulfinic and sulfenic acids. Although the dipolaric resonance formula of 3 explains the electrophilic character with regard to methylation (formation of 8, 12) no nucleophilic character at carbene carbon atom could be proved by trapping experiments with electron poor systems like dimethyl fumarate or acetylene dicarboxylate.

Trapping reactions with diazoalkanes

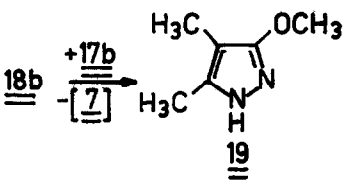
Direct trapping experiments of sulfur (and other) substituted carbenes have been described with diaryl-diazomethanes[11]. The high self-decomposition tendency of carbenes 3 demands diazoalkanes of higher reactivity for trapping. In the present cases diazomethane (17a) and diazoethane (17b) have been found to be excellent trapping agents especially under PTC conditions (50% KOH, diethyl ether, 18-crown-6):

Scheme 5: Trapping of carbenes 3 by diazoalkanes 17



	R^3
17a	H
b	CH_3

	R^1	R^2	R^3
18a	4-$CH_3C_6H_4$	CH_3	H
b	"	CH_3	CH_3
c	"	C_2H_5	H

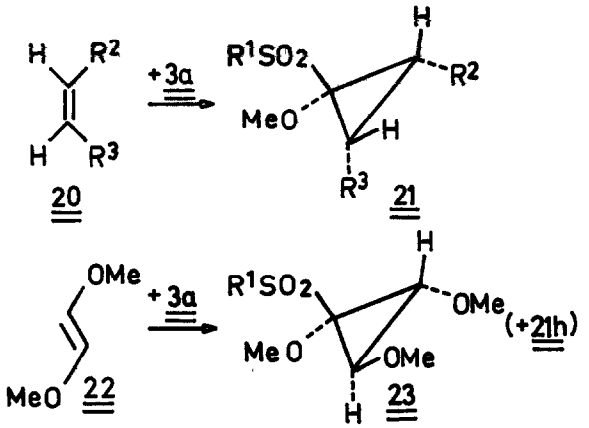


Whereas 17a leads to the unreactive vinylsulfone 18a[12], 17b yields the more polar 18b as a mixture of isomers (Z/E = 15:85) which is trapped with excess 17b by 1,3-dipolar cycloaddition and aromatization (under elimination of 7) yielding pyrazole 19.

Trapping reactions with electron rich olefins[13]

To prevent nucleophile-catalyzed self-decomposition of 3 sufficiently reactive olefins must be used for cyclopropanation. Scheme 6 compiles the generated cyclopropyl sulfones 21 and 23 resulting from corresponding enol ethers and styrenes 20 and 22.

Scheme 6: Trapping of carbene 3a with olefins 20, 22



3a, 21, 23: R^1=4-$CH_3C_6H_4$

		R^2	R^3
20, 21	a	H	OMe
	b	H	OEt
	c	H	OBu
	d	H	Ph
	e	H	4-$MeOC_6H_4$
	f	-CH_2-CH_2-O-	
	g	- O -CH_2 - O -	
	h	OMe	OMe

As anticipated result of structural investigations it should be mentioned that sulfonyl substituents avoid vicinal ether (and aryl) groups in cis position of cyclopropane rings if possible. Only in the presence of a threefold excess of (E)-1,2-dimethoxy-ethylene (22 : 99.1/0.9 E:Z) and by deprotonation at -75°C with n-BuLi in THF cyclopropane 23 (31% yield) containing a vicinal cis-methoxy group with respect to the sulfonyl group and no detectable amount of 21h is found; at the same time the isomer ratio 22:20h of excess olefin drops to 16:1. Under PTC conditions at 0°C - sixfold excess of 22, immediate mixing of all components - a 26% yield of 23 and already 1% 21h (3:2 E/Z ratio of non-consumed olefin) are observed; at 25°C and dropwise addition of a solution of 1a only 10% 23 together with 29% 21h (1:3 E/Z ratio of nonconsumed olefin) are registrated. On the other hand, trapping reaction of carbene 3a (PTC conditions, room temp., dropwise addition of a sixfold excess of an 1:3 E/Z olefin mixture) with (Z)-1,2-dimethoxyethylene yields exclusively 83% of 21h. These results give further insight in the cyclopropanation[14] reactions mentioned before. Carbenes with π-donor substituents are supposed to be singlet carbenes, the sulfonyl group should not vary this tendency[15]. This acceptance would fit with the described results although cases are mentioned in which singlet carbenes (i.e. fluorenylidene[16]) add stereospecifically only to the thermodynamically more stable olefin isomer whereas the thermodynamically less stable isomer yields a mixture of stereoisomeric cyclopropanation products. The stereospecific cycloaddition of 3a to Z- and E-1,2-dimethoxyethylene proves to be of particular interest. The more stable Z-isomer[29] adds faster than the E-isomer. However, starting with 99% E-isomer in excess and regarding the temperature dependent E/Z ratio as well as the final isomer ratio of non-consumed olefin, one could draw the conclusion that an intermediate carbene-olefin complex is reversibly formed yielding either stereospecifically cyclopropane 23 - favored by low temperature - or forming back carbene 3a and olefin with subsequent formation of 21h - favored at higher temperature. In the course of this reverse reaction the non-consumed olefin part becomes obviously more or less isomerized depending

on reaction conditions up to the known[29] 1:3 E/Z equilibrium mixture. Comparable observations have been made with dihalocarbenes and trans-cyclooctene[17]. By an independent experiment in the presence of all reaction components excepted carbene 3a (PTC conditions, room temp., stirring for 2 days) the E/Z ratio of the starting olefin remains nearly unchanged (enhancement of Z part from 2.4 to 2.7%).

Stereochemistry of cycloadditions

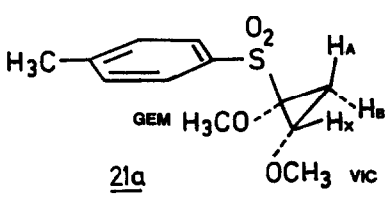
In the course of preceding ^1H NMR shift experiments[3b)12] it could be shown that β and γ hydrogens of 1-arylsulfonyl 1-methoxy alkenes cis to sulfonyl groups occur at lower field than the corresponding trans hydrogens (in vinyl as well as in allyl position). The replacement of the double bond by a cyclopropane ring should not change these phenomena principally even if opposite assignments in cyclopropyl sulfones have been reported[18]. ^1H NMR shift experiments with 21a using $Eu(FOD)_3$ exhibit the strongest shifting (that is the strongest slope of the shifting straight line) at H_X. On basis of this value the relative slopes for the other hydrogens are:

H_X	H_A	o-H_{ar}	H_B	H_3CO_{gem}	H_3CO_{vic}	m-H_{ar}	p-CH_3	
(3.813)	(1.917)	(7.819)	(1.426)	(3.693)	(3.144)	(7.372)	(2.455)	δ,ppm
1	0.87	0.71	0.63	0.54	0.24	0.09	0.01	

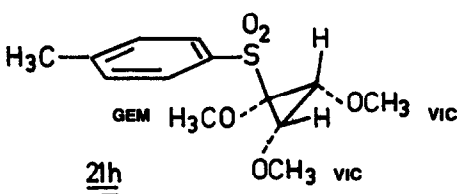
The assignments by these measurements are in accordance with those given for several (4-methoxyphenylsulfonyl)cyclopropanes[19]. The corresponding shift experiments with 21h give the following result. These values are according to those of 21a.

$H_{cycloprop.}$	H_3CO_{vic}	H_3CO_{gem}	o-H_{ar}	m-H_{ar}	p-CH_3	
(3.795)	(3.348)	(3.879)	(7.883 - 7.264)		(2.461)	δ,ppm
1	0.40	0.38	0.29	0.13	0.07	

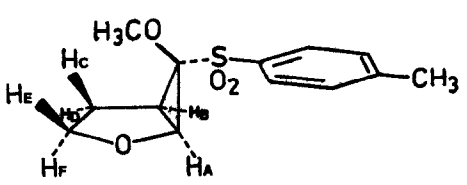
Scheme 7: Structural assignments of 21a, 21h, 21f and 21g



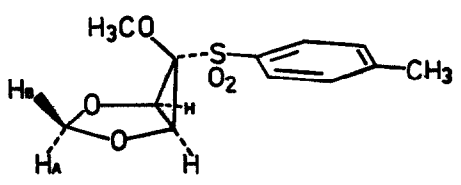
21a



21h



21f



21g

The structure of 21f is elucidated by means of high resolution ^1H NMR technique using a 2D experiment and COSY 45 method[20a]. Starting from H_A as the aliphatic hydrogen at lowest field the COSY 45 plot gives the hydrogen shifts of the other aliphatic hydrogens as well as their coupling constants:

H_A	H_B	H_C	H_D	H_E	H_F	
4.733	2.459	2.040	2.224	3.756	4.176	δ,ppm

J_{AB}	J_{BC}	J_{BD}	J_{CD}	J_{CE}	J_{CF}	J_{EF}	
6.6	-	6.5	-12.8	8.7	4.1	-8.3	Hz;±0.5
6.5	-	6.5	-12.8	8.3	4.1	-8.1	

Consequently, the configuration of cyclopropanation product 21f of a cyclic enol ether corresponds to that of 21a.

In order to assign the configuration of 21g, ^1H NMR NOE technique has been applied[20b]. Of the two geminal hydrogens H_A(δ=5.447) and H_B(δ=5.090; J_{AB} = -2.1 Hz) only H_B exhibits a positive (approx. 1%) NOE during irradiation with the methoxy frequency (δ =3.859) and vice versa. As expected the aromatic ortho hydrogens show the same effect, surprisingly also the two vicinal cyclopropane hydrogens through the three-membered ring; they occur as singlet (δ=4.749) at nearly the same field as H_A of 21f (δ=4.733).

Finally, having assigned the configurations of 21a, 21f, 21g, and 21h by three independent methods, all other cyclopropanes are structurally assigned by comparison with these confirmed structures.

EXPERIMENTAL

Melting points were determined throughout using a Fus-O-mat[21] of Heraeus. Elemental analyses were obtained by the ultramicro method[22] and were in agreement with the calculated values. Infrared spectra were recorded on Beckman IR 4230 or IR 33 spectrometers. ^1H and ^{13}C NMR spectra were recorded on Bruker WH 90 and AM 400 spectrometers from $CDCl_3$ solutions (TMS as internal standard). GC investigations were carried out using a Hewlett-Packard 5750 G gas-chromatograph, TLC investigations ensued on foils Alugram ^{R} Sil G/UV_{254} of Macherey and Nagel, and the 1:3 E/Z mixture of isomers of 1,2-dimethoxyethylene was separated by use of a micro spinning band column of Normag (100 cm length, 1200 cpm). Carbon monoxide formation had been proved by use of aqueous $PdCl_2$ as well as by CO 10a test tubes of Dräger.[23]

(Alkoxy)(halo) methyl 4-tolyl sulfones 1: 1a and 1b were synthesized according to the known method[3a], except that the volume of solvent applied was doubled. The formation of 1f from 1b by the described method[7] was established. 1c was prepared in analogy to 1a, 1b[3a] starting from -ethoxy- -tosylacetophenone[24]; bromination ensued with 83% yield furnishing the intermediate bromoketone (m.p. 94°C, recrystallized from petrol ether), subsequent acyl cleavage yielded 40% (bromo)(ethoxy) methyl 4-methylphenylsulfone (1c), $C_{10}H_{13}BrO_3S$(293.2): m.p. 158°C (from methanol); IR(KBr): 1593 (aryl); 1340/1335/1321; 1158/1142 (sulfonyl) cm^{-1}; ^1H NMR ($CDCl_3$): δ=8.01-7.30 (m,4H,H_{ar}); 6.41 (s,1H,CH); 4.13-3.49 (m,2H,OCH_2); 2.50(s,3H,p-CH_3);

1.21(t,3H,CH_3; J=7.3 Hz).

Generation and self-decomposition of carbene 3a (method B), qualitative determination of decomposition products:

a) 1.2 g 1a or 1.4 g 1b (5 mmol) were dissolved in 15 ml anhydrous THF (or DMF) under dry nitrogen and a very slow (!) nitrogen stream was bubbled through the solution. 0.7 g (6.3 mmol) Potassium tert.-butylate dissolved in 15 ml anhydrous THF was added dropwise to the stirred solution at room temp., and the gas stream escaping from the reaction mixture was passed through an aqueous $PdCl_2$ solution (formation of elemental palladium) or through a Dräger test tube CO 10/a[23] indicating evolution of carbon monoxide (6) from the reaction mixture. The precipitate consisting of potassium halide and potassium 4-toluenesulfinate (4a) was filtered off, dissolved in 5 ml of water, and therein, 4a was proved by use of aqueous permanganate. TLC investigation of the filtrate proved the presence of methyl 4-toluenesulfinate (8a), di-4-tolyl disulfide (9a), S-(4-methylphenyl) 4-methylbenzenethiosulfonate (10a), methoxy-di(4-methylphenylsulfonyl)methane (11a) and traces of 1-methoxy-1,1-di(4-methylphenylsulfonyl)ethane (12a), identified by comparison with independently prepared samples. Attempts to separate the reaction mixture by column chromatography using SiO_2 as well as neutral Al_2O_3 failed in consequence of partial decomposition. Therefore, the filtrate was evaporated i.vac. yielding an oil from which 11a crystallized, impurified by small amounts of 12a, after addition of 1 ml of ether. Filtration, washing with ether and recrystallization from methanol yielded 200 mg (23%) of pure 11a, m.p. 165°C (166°C, ref.[4]).

b) If the same experiment was carried out at 60°C all reaction products could be proved again, however, the part of 12a was increased on costs of 11a. After addition of ether as before, 12a crystallized as the first fraction and was free of impurities after washing with excess ether; yield 80 mg (8%), m.p. 130°C. 11a crystallized after cooling from the mother liquor; yield up to 450 mg (52%), m.p. 165°C.

Independent synthesis of 1-methoxy-1,1-di(4-methylphenylsulfonyl)ethane (12a) by methylation of 11a: 1.06 g (3 mmol) 11a dissolved in 60 ml anhydrous THF were added dropwise under stirring to a solution of 0.4 g (3.6 mmol) potassium tert.-butylate in 60 ml anhydrous THF. 0.7 g (4.9 mmol) methyl iodide dissolved in 10 ml anhydrous THF was added and stirring was continued for 2 h. The reaction mixture was poured onto ice water, neutralized with diluted hydrochloric acid, and extracted three times with chloroform. After drying with $MgSO_4$ the solvent was evaporated i.vac. and crystallization of the residue was caused by addition of a few drops of ether; yield 700 mg (63%) of 12a, $C_{17}H_{20}O_5S_2$ (368.5), m.p. 130°C (copper block); IR(KBr): 1340, 1155 (sulfonyl) cm^{-1}; ^1H NMR ($CDCl_3$): δ=8.0-7.1 (m,8H,H_{ar}), 3.60 (s,3H,OCH_3), 2.45 (s,6H,p-CH_3), 1.93 (s,3H,CH_3).

4-Chlorophenylsulfonyl-methoxy-4-methylphenylsulfonylmethane (11c): 5.0 g (25 mmol) sodium 4-chlorobenzenesulfinate and 80 mg (0.3 mmol; 6%) 18-crown-6 phase transfer catalyst were added to 10 ml of 50% aqueous KOH. 1.0 g (4.3 mmol) 1a, dissolved in 20 ml THF and diluted with 40 ml ether, was added dropwise under stirring at room temp., and stirring was continued for 12 h. The reaction mixture was then diluted with 100 ml water, acidified with dilute hydrochloric acid and extracted for several times with chloroform. After drying the chloroform phase over $MgSO_4$ and concentrating i.vac. 650 mg (40%) 11c crystallized from the solution; m.p. 182°C after recrystallization from methanol (m.p.[4] 186°C). All spectroscopic data were in agreement with those of a sample obtained by an alternative route[4].

1-Methoxy-1-(4-methylphenylsulfonyl)ethylene (18a): 10 ml of 50% aqueous KOH, 80 mg (0.3 mmol; 6%) 18-crown-6 and an ethereal solution of diazomethane (17a), prepared according to the usual procedure[25] from 10 g (110 mmol) N-nitroso-N-methylurea, were cooled to -10°C. Under vigorous stirring a solution of 1.2 g 1a (or 1.4 g 1b) (5 mmol) in 20 ml THF, diluted with ether onto a volume of 60 ml, was dropped to this mixture over a period of several hours (the slower the better the yield). After stirring for 12 h, 100 ml water were added, excess 17a was decomposed by addition of ethereal hydrogen chloride until the yellow color disappeared; the ethereal phase was separated and the aqueous phase was extracted twice with ether. The combined ether extracts were dried over $MgSO_4$, ether was distilled off, at last i.vac., and the oily residue was dissolved in a small amount of methanol. After cooling to -25°C, 0.8 g (76%) 18a were obtained as white crystals of m.p. 99°C (m.p.[12] 97°C). All spectroscopic data were in accordance with those of a sample prepared by an alternative method[12].

1-Ethoxy-1(4-methylphenylsulfonyl)ethylene (18c): 1.5 g (5.1mmol) 1c were converted by the same procedure as described before. Extremely slow addition of the solution of 1c to the two-phase system in the course of 10-12 h gave yields of 18c up to 80% and only traces of 8 and 11b as by-products. Faster addition within about 1 h yielded after work-up a crystalline mixture of 8, 11b and 18c from which 8 and 11b were separated by repeated washings with ether. The yield of 8 was determined by ^1H NMR spectroscopy from mother liquor as 8%. Evaporation of ether, addition of a small amount of methanol and cooling to -25°C yielded 350 mg (30%) of 18c, m.p. 52°C (m.p.[12] 53°C). The residue on the filter consisted of 250 mg (26%) of pure ethyl di(4-methylphenylsulfonyl)methyl ether (11h), $C_{17}H_{20}O_5S_2$(368.5); m.p. 168-169°C (from methanol); IR(KBr): 1591 (Aryl), 1340/1332, 1158/1137 (Sulfonyl) cm^{-1}; ^1H NMR ($CDCl_3$): δ=7.98-7.37 (m,8H,H_{ar}), 5.16 (s,1H,CH), 3.83 (q,2H,OCH_2; J=7 Hz), 2.48 (s,6H,p-CH_3), 1.08 (t,3H,CH_3; J=7 Hz).

Z,E-1-Methoxy-1-(4-methylphenylsulfonyl)-1-propene (18b) and 1H-3-methoxy-4.5-dimethylpyrazole (19):

a) 1.2 g (5 mmol) 1a were converted to carbene 3a in presence of excess diazoethane (17b)[16] as described before. Solvent was evaporated, the residue was purified from polymers by dissolving in methylene chloride and chromatography through a short SiO_2 column. After evaporation 250 mg (22%) of a 15:85 Z/E-mixture of 18b (determined by ^1H NMR spectroscopy) crystallized. Repeated crystallizations from methanol furnished pure E-isomer of 18b, $C_{11}H_{14}O_3$ (226.3), m.p. 60°C; IR(KBr): 1650 (C=C), 1592 (aryl), 1320, 1161/1123 (sulfonyl) cm^{-1}; ^1H NMR ($CDCl_3$): δ=7.94-7.30 (m,4H,H_{ar}), 6.54 (q,1H,CH;J=7 Hz), 3.84 (s,3H,OCH_3), 2.46 (s,3H,p-CH_3), 1.80 (d,3H,CH_3;J=7 Hz).

The Z-isomer of 18b could not be isolated in pure state, but its characteristic signals in ^1H NMR could be measured[27]: δ=7.94-7.30 (m, 4H, H_{ar}), 5.42 (q, 1H, CH; J=7Hz), 3.62 (s, 3H, OCH_3), 2.46 (s, 3H, p-CH_3), 2.15 (d, 3H, CH_3; J=7Hz).

b) A corresponding batch starting from 2 g (8.5 mmol) 1a yielded a residue from which 500 mg 19 could be separated by sublimation (0.02 Torr, 50°C); m.p. 88-90°C (sublimation, measured on a Kofler apparatus; m.p.[28] 85°C).

Cyclopropanations of olefins 20 and 22 by carbene 3a.

Method A. 3 ml (5 mmol) of a 15 per cent solution of n-butyllithium in n-hexane were added dropwise very slowly to a solution of 1.3 g (15 mmol) 22 (purity 99.1%) and 1.17 g (5 mmol)

1a in 100 ml anhydrous THF under dry nitrogen. After stirring for 24 h (TLC control) and warming-up to room temp., 100 ml water were added. The reaction mixture was extracted with ether for several times, dried over $MgSO_4$, and the solvent was distilled off. The crystalline residue (550 mg) consisted of a 5:1 mixture of 1-(4-methylphenylsulfonyl)-1-trans,2-trans,3cis-trimethoxycyclopropane (23) (31%) and 11a from which pure 23 could be obtained by fractionated recrystallizations, m.p. 90°C (methanol); $C_{13}H_{18}O_5S$ (286.3), M^+ at m/z 286; IR(KBr): 1598 (Aryl), 1326/1298, 1158 cm^{-1} (Sulfonyl); ^1H NMR ($CDCl_3$):δ=7.961-7.260 (m,4H,H_{ar}), 4.313 (d,1H,$H_{cyclopropyl}$; J=3.6 Hz), 3.764 (d,1H,$H_{cyclopropyl}$; J=3.8 Hz), 3.72 (s,3H,OCH_3 gem), 3.576 (s,3H,OCH_3), 3.159 (s,3H,OCH_3), 2.451 (s,3H,p-CH_3); ^{13}C NMR ($CDCl_3$/TMS): δ=144.75, 135.90, 129.56, 128.84 (C_{ar}), 82.81 (C1), 70.09, 68.77, 59.18 (CH, OCH_3), 21.65 (p-CH_3). The E/Z ratio of non-consumed olefin was 16:1 at the end of the reaction.

Method C. 2.6 g (30 mmol) of an olefin mixture 20h/22 (3:1)[29] and 80 mg 18-crown-6 in 100 ml ether were combined with 10 ml 50 per cent aqueous KOH. A solution of 1.17 g (5 mmol) 1a in 10 ml THF and 40 ml ether was dropped to this mixture at room temp. very slowly (6-8h) under vigorous stirring, and stirring was continued for 12h. After complete conversion of 1a (TLC control), 100 ml water were added and work-up ensued as described before. The obtained crystalline mixture (1.26 g, 83% 21h and 8% 11a) was recrystallized from methanol, yielding pure 1-(4-methylphenylsulfonyl)-1,2,3alltrans-trimethoxycyclopropane (21h), m.p. 95°C, $C_{13}H_{18}O_5S$ (286.3), M^+ at m/z 286; IR(KBr): 1590 (Aryl), 1325/1310, 1150/1140 cm^{-1} (sulfonyl); ^1H NMR ($CDCl_3$): δ=7.883-7.264 (m,4H,H_{ar}), 3.879 (s,3H,OCH_3 gem), 3.795 (s,2H,$H_{cyclopropyl}$), 3.348 (s,6H,OCH_3), 2.461 (s,3H,p-CH_3); ^{13}C NMR ($CDCl_3$/TMS): δ=144.92-127.83 (C_{ar}), 75.641 (C1), 62.317, 60.302, 59.912 (CH,OCH_3), 21.63 (p-CH_3).

By this method C further cyclopropanes 21 were prepared: 1-trans,2-trans-dimethoxy-1-(4-methylphenylsulfonyl)cyclopropane (21a), reaction conditions: threefold excess 20a, 0°C, 2d; yield 72%, m.p. 82°C (methanol), $C_{12}H_{16}O_4S$ (256.3); IR(KBr): 1593 (aryl), 1312/1300/1288, 1150/1132 cm^{-1} (sulfonyl); ^1H NMR ($CDCl_3$/TMS): δ=8.0-7.38 (m,4H,H_{aryl}); 3.88 (dd,1H,H_X; J=5/8 Hz), 3.73 (s,3H,OCH_3), 3.19 (s,3H,OCH_3), 2.49 (s,3H,p-CH_3), 1.93 (dd,1H,H_A; J=8/-8 Hz), 1.43 (dd,1H,H_B; J=5/-8 Hz); ^{13}C NMR ($CDCl_3$/TMS): δ=144.80, 134.60, 129.66, 128.77 (C_{ar}), 78.33 (C1), 62.67 (C2), 59.46, 59.18 (OCH_3), 21.67 (p-CH_3), 16.74 (C3).

2-trans-Ethoxy-1-trans-methoxy-1-(4-methylphenylsulfonyl)cyclopropane (21b), reaction conditions: Twofold excess 20b, room temp., 1d; yield 75.5%, m.p. 35.7°C (methanol), $C_{13}H_{18}O_4S$ (270.3); IR(KBr): 1595 (Aryl), 1320, 1140 cm^{-1} (Sulfonyl); ^1H NMR($CDCl_3$/TMS): δ=7.807, 7.367 (d,2H,H_{ar}; J=8.3 Hz), 3.876 (dd,1H,H_X; J=5.2/8.2 Hz), 3.681 (s,3H,OCH_3), 3.242, 3.350 (qd, 1H,CH_2; J=7.1/-9.3 Hz), 2.458 (s,3H,p-CH_3), 1.913 (dd,1H,H_A; J=8.1/-8.1 Hz), 1.426 (dd,1H,H_B; J=5.1/-8.1 Hz), 1.070 (t,3H,CH_3; J=7.0 Hz); ^{13}C NMR($CDCl_3$/TMS): δ=144.74, 134.78, 129.66, 128.79 (C_{ar}), 78.44 (C1), 67.32 (CH_2), 61.09 (C2), 59.41 (OCH_3), 21.65 (p-CH_3), 16.77 (C3), 14.75 (CH_3).

2-trans-(n-Butoxy),1-trans-methoxy-1-(4-methylphenylsulfonyl)cyclopropane (21c), reaction conditions: Twofold excess 20c, room temp., 2d; yield 23%, m.p. 39.3°C (methanol), $C_{15}H_{22}O_4S$ (298.4); IR(KBr): 1595 (Aryl), 1310, 1135 cm^{-1} (Sulfonyl); ^1H NMR($CDCl_3$/TMS): δ=7.807, 7.364 (d,2H,H_{ar}; J=8.3 Hz), 3.859 (dd,1H,H_X; J=5.1/8.2 Hz), 3.673 (s,3H,OCH_3), 3.256, 3.175 (td,1H, OCH_2; J=6.7/-9.4 Hz), 2.453 (s,3H,p-CH_3), 1.903 (dd,1H,H_A; J=8.2/-8.0 Hz), 1.417 (dd,1H,H_B; J=5.1/-8.0 Hz), 1.393 (m,2H,β-CH_2), 1.226 (m,2H,γ-CH_2), 0.819 (t,3H,CH_3; J=7.3 Hz); ^{13}C NMR ($CDCl_3$/TMS): δ=144.71, 134.74, 129.60, 128.77 (C_{ar}), 78.42 (C1), 71.66 (OCH_2), 61.20 (C2),

59.40 (OCH_3), 31.16 (β-CH_2), 21.63 (p-CH_3), 19.00 (-CH_2), 16.80 (C3), 13.62 (CH_3).
1-trans-Methoxy-2-trans-phenyl-1-(4-methylphenylsulfonyl)cyclopropane (21d) and 1-trans-methoxy-2-trans-(4-methoxyphenyl)-1-(4-methylphenylsulfonyl)cyclopropane (21e): These compounds were obtained - using a threefold excess of 20 - in minor amounts (10 resp. 15%) as crude products from which only ^{1}H NMR spectra ($CDCl_3$/TMS) were recorded; main product was disulfone 11a (43 resp. 48%). 21d ($C_{17}H_{18}O_3S$; 302.4): δ=7.896-7.202 (m,9H,H_{ar}), 3.485 (s,3H,OCH_3), 3.237-3.057 (m,1H,H_X), 2.45 (s,3H,p-CH_3), 2.18-2.01 (m,1H,H_A), 1.74-1.564 (m,1H,H_B).
21e ($C_{18}H_{20}O_4S$; 332.4): δ=7.890-6.817 (m,8H,H_{ar}, 3.752 (s,3H,p-OCH_3), 3.478 (s,3H,OCH_3), 3.255-3.009 (m,1H,H_X), 2.455 (s,3H,p-CH_3), 2.167-1.99 (m,1H,H_A), 1.669-1.503 (m,1H,H_B).
endo-6-Methoxy-exo-6-(4-methylphenylsulfonyl)-2-oxabicyclo[3.1.0]hexane (21f), reaction conditions: Sixfold excess 20f, room temp., 4d; yield 48%, m.p. 129.4 (methanol), $C_{13}H_{16}O_4S$ (268.3); IR(KBr): 1595 (Aryl), 1300, 1155 cm^{-1} (Sulfonyl); ^{1}H NMR($CDCl_3$/TMS): see theoretical part; ^{13}C NMR($CDCl_3$/TMS): δ=144.71, 134.95, 129.75, 128.56 (C_{ar}), 80.15 (C6), 71.94 (C3), 65.56 (C1), 59.90 (OCH_3), 29.51 (C5), 25.06 (C4), 21.63 (p-CH_3).
endo-6-Methoxy-exo-6-(4-methylphenylsulfonyl)-2,4-dioxabicyclo[3.1.0]hexane (21g), reaction conditions: Threefold excess 20g, 0°C, 1.5d; yield 18.5%, m.p. 124.9 (methanol), $C_{12}H_{14}O_5S$ (270,3); IR(KBr): 1595 (Aryl), 1300, 1155 cm^{-1} (sulfonyl); ^{1}H NMR($CDCl_3$/TMS): see theoretical part; ^{13}C NMR($CDCl_3$/TMS): δ=145.32, 134.25, 129.95, 128.65 (C_{ar}), 103.12 (C3), 78.91 (C6), 62.0 (C1,C5), 60.02 (OCH_3), 21.68 (p-CH_3).

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