Tetrahedron Letters,Vol.23,No.41,pp 4203-4206,1982 0040-4039/82/414203-04$03.00/0
Printed in Great Britain

A NEW SULFENE SYNTHESIS

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Abstract. Treatment of trimethylsilylmethanesulfonyl chloride with cesium fluoride in acetonitrile at room temperature has been found to produce sulfene which can be trapped in good yield.

The most widely used procedure for the generation of sulfene involves the treatment of methanesulfonyl chloride with triethylamine.[1] While adducts of sulfene, generated by this route, can usually be isolated in satisfactory yield, the amine or its acid salt may isomerize or decompose base- or acid-sensitive reaction partners. Furthermore the interpretation of reaction mechanisms can sometimes be complicated by the presence of the amine. Thus the amine may form a complex with sulfene prior to its reaction with other substrates.[2] We wish to report a simple new procedure for the generation of sulfene which avoids the use of amines and at the same time gives excellent yields of adducts under gentle, neutral reaction conditions. In this method, illustrated in eq 1, sulfene is formed in the presence of a trapping agent by fluorodesilylation of trimethylsilylmethanesulfonyl chloride (1).

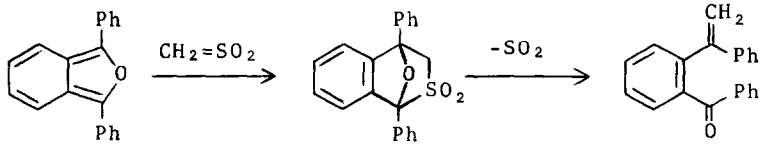
$$(CH_3)_3SiCH_2SO_2Cl + F^- \longrightarrow CH_2{=}SO_2 + (CH_3)_3SiF \qquad (1)$$

1

$$(CH_3)_3SiCH_2Cl \xrightarrow[2)\ Cl_2,\ H_2O,\ 0^\circ]{1)\ (NH_2)_2C{=}S,\ EtOH} (CH_3)_3SiCH_2SO_2Cl \qquad (2)$$

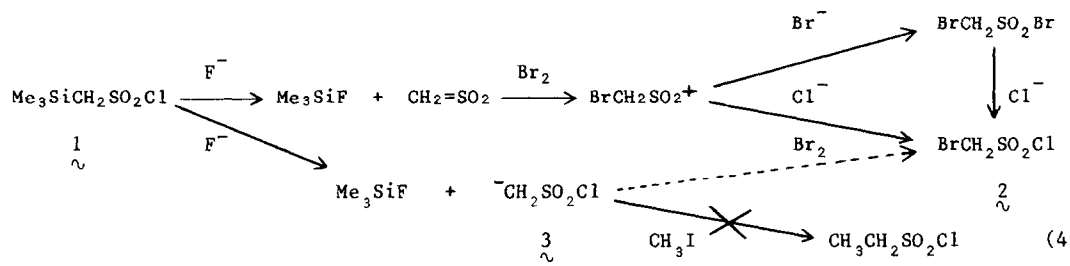
We have found that the known[3] reagent 1 can be conveniently synthesized in 58% overall yield via chlorination of an aqueous solution of the isothiuronium salt formed by refluxing a mixture of chloromethyltrimethylsilane and thiourea in ethanol (see eq 2 and experimental below). When a solution of 1 together with an equivalent amount of cesium fluoride, flame-dried in place prior to use, was stirred in dry acetonitrile at room temperature for two hours in the presence of various sulfene trapping agents, sulfene adducts could be isolated in yields which were in all cases superior to those obtained using mesyl chloride/triethylamine as the source of sulfene (see Table). Particularly notable is our observation that cyclopentadiene, which fails to yield an adduct with sulfene produced by mesyl chloride-triethylamine,[4,5] cleanly affords the adduct 2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide in 64% yield when 1 is treated with cesium

fluoride in the presence of cyclopentadiene. The structure of the previously unknown sulfene-cyclopentadiene adduct was established spectroscopically[6] and by lithium aluminum hydride reduction to the known[7] 2-thiabicyclo [2.2.1] hept-5-ene. Attempted trapping by 2,6-diphenyl-isobenzofuran of sulfene prepared via eq 1 led instead to 1,1-phenyl (o-benzoyl)phenyl ethylene,[8] presumably by desulfonylation of the initial Diels-Alder adduct (eq 3).



(3)

Generation of sulfene from 1 in the presence of bromine led to a mixture of bromomethane-sulfonyl bromide[10] and bromomethanesulfonyl chloride (2).[9] Control experiments established that 1 does not react with bromine in the absence of cesium fluoride and that chloride ion rapidly converts bromomethanesulfonyl bromide to 2 (see eq 4). When 1 was treated with cesium fluoride and bromine in the presence of excess tetraethylammonium chloride, 2 could be isolated in 79%



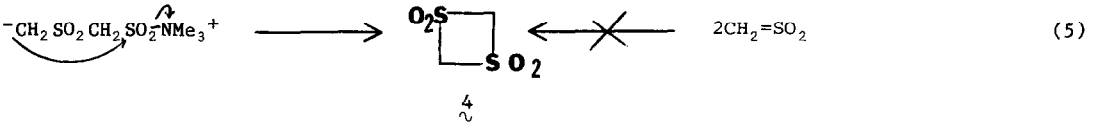
(4)

yield. An alternative route to 2 involving bromination of carbanion 3 could be ruled out since fluorodesilylation of 1 in the presence of excess methyl iodide failed to afford ethanesulfonyl chloride. It should be noted that bromination of sulfene produced from mesyl chloride/triethyl-amine cannot be accomplished due to competitive bromine-amine adduct formation.

A limitation of our fluorodesilylation sulfene synthesis is illustrated by the trapping reaction with N,N-diethylamino-1-propyne which gives the same 1:1 mixture of 2-methyl-3-(N,N-diethylamino)thiete 1,1-dioxide and 4-methyl-3-(N,N-diethylamino)thiete 1,1-dioxide obtained with mesyl chloride/triethylamine,[11] albiet in superior yield. Separate experiments established that fluoride ion equilibrated samples enriched in one of these isomers.

Sulfene produced according to eq 1 in the absence of trapping agents failed to afford detectable amounts of the sulfene "dimer" 1,3-dithietane 1,1,3,3-tetraoxide (4).[12] Based on this observation we propose that the formation of 4 from the reaction of mesyl chloride with

trimethylamine[12] involves cyclization of a dimeric amine complex (see eq 5)[2] rather than direct sulfene cyclodimerization.[13]



(5)

We suggest that fluorodesilylation of 1 affords sulfene via a concerted E_2-elimination process akin to that involved in olefin formation from fluorodesilylation of β-halosilanes.[14] The present work provides the first instance of generation of a carbon-hetero multiple bond via fluorodesilylation and opens up new avenues for the study of sulfene chemistry.

Acknowledgement. We are indebted to the National Science Foundation (CHE 80-01490) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of these investigations.

References and Footnotes

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5. In our hands reaction of cyclopentadiene with mesyl chloride/triethylamine led to a complex mixture with only traces of the cyclopentadiene-sulfene adduct.

6. ^{1}H NMR ($CDCl_3$) δ6.3 (m, 2H), 3.8 (br s, 1H), 3.4 (br s, 1H), 2.9 (m, 1H), 2.6 (m, 1H) and 2.38 ppm (br s, 2H); ^{13}C NMR ($CDCl_3$) δ140.8 (d), 129.6 (d), 64.8 (d), 47.8 (t), 45.4 (t), 41.3 ppm (d); IR (film) 1700 (m), 1298 (vs), 1222 (s), 1161 (s), and 1138 cm^{-1} (vs); MS 144.

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8. Mp 108-109°C (from hexane); ^{1}H NMR ($CDCl_3$) δ7.58-6.8 (m, 14H), 5.35 (d, 1H, J = 0.5 Hz), 5.12 (d, 1H, J = 0.5 Hz), ^{13}C NMR ($CDCl_3$) δ197.7, 148.6, 141.2, 140.6, 137.4, 132.6, 130.5, 130.1-127.3 (sev. peaks), 116.6 ppm.; IR 1660 (vs), 1598 (s), 1282 (vs), 925 (s), 700 (vs) cm^{-1}; Anal., Calcd for $C_{21}H_{16}O$, C 88.78, H, 5.67, Found C 88.16, H 5.64.

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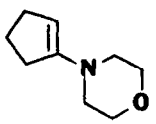
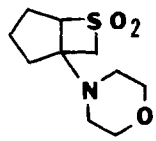
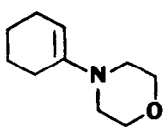
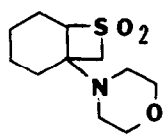
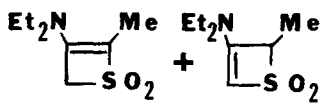
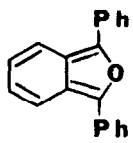
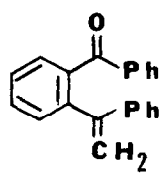
Table: Sulfene Adducts from Fluorodesilylation of Trimethylsilylmethanesulfonyl Chloride

Entry	Substrate	Product	Yield	Yield with MsCl/Et_3N
1			81%	77%[1]
2			65%	54%[1]
3	$MeC{\equiv}CNEt_2$	 (1 : 1)	90%	66%[11]
4			69%	ca. 0%[4,5]
5			92%	--
6	$Br_2/Et_4N^+ Cl^-$	$BrCH_2SO_2Cl$	79%	N.R.

Preparation of Trimethylsilylmethanesulfonyl Chloride (1):

Chlorotrimethylsilane (12.3 g, 0.1 mol), thiourea (15.6 g, 0.2 mol) and ethyl alcohol (175 mL) were heated to reflux for 48 h. Concentration gave a solid which was dissolved in 200 mL of water, cooled in ice, and treated with chlorine via a bubbler with vigorous stirring during 15 min at temperatures below 25° C. Methylene chloride (150 mL) was added and chlorine was then bubbled in for an additional 0.5 h. The organic layer was separated and the aqueous layer was extracted with methylene chloride (50 mL). The combined organic extract was washed with cold 10% $NaHSO_3$ solution, 10% $NaHCO_3$ solution and finally with water. The organic layer was dried and concentrated in vacuo affording 10.8 g (58% yield) of the title compound as a colorless liquid, bp 50-52°C (0.6 mm), ^1H NMR ($CDCl_3$) δ3.32 (s, 2H), 0.18 (s, 9H).

Preparation of 2-Thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide:

Cesium fluoride (1.0 g, 6.06 mmol) was placed in a two-necked flask equipped with a three-way stopcock, septum, and spinbar and the salt was flame-dried under vacuum and cooled under argon. Acetonitrile distilled from P_2O_5 (30 mL) and freshly prepared cyclopentadiene (1.4g, 21.6 mmol) were added via syringe. The flask was cooled to 0°C and a solution of 1 (1.0 g, 5.4 mmol) in 10 mL of dry acetonitrile was added to the flask dropwise with stirring. Stirring was continued for 2 h at room temperature. The reaction mixture was concentrated in vacuo, and the product taken up in methylene chloride. The organic layer was washed with water, dried, and concentrated in vacuo affording 2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide as a thick, thermally unstable oil (0.5 g; 64% yield) of good purity as indicated by spectral analysis.[6]

(Received in USA 30 June 1982)