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STABLE SULFINIC ACIDS FROM THE ENE REACTION OF METHYL-SUBSTITUTED ALLENES WITH SULFUR DIOXIDE

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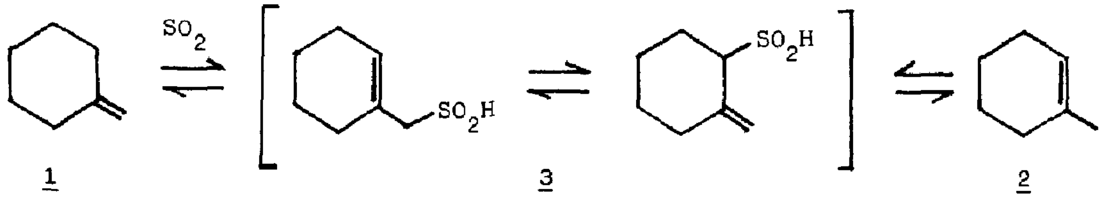
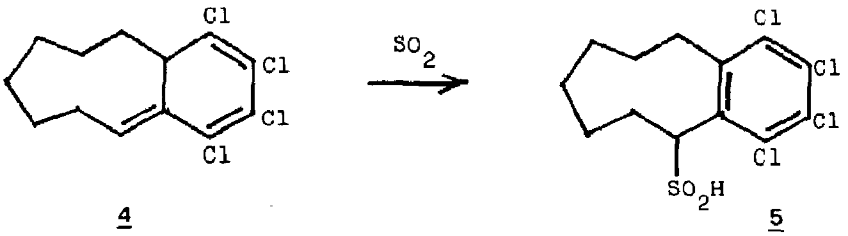
Summary. Allenes 2,4-dimethyl-2,3-pentadiene and 3-methyl-1,2-butadiene in liquid sulfur dioxide undergo ene addition with the solvent giving the stable 3-(2,4-dimethyl-1,2-pentadienyl) and 2-(3-methyl-1,2-butadienyl) sulfinic acids.

ENE and retro-ene reactions, with the intermediacy of the allylic sulfinic acids 3, ha been proposed to account for the allylic isomerization of alkenes 1 and 2 in the presence of sulfur dioxide[1] (eq 1), as well as for the sulfur dioxide-catalized deuteriation with deuterium oxide of a number of olefinic compounds (among which alkenes 1 and 2)[2].



(1)

However, direct observation and isolation of the intermediate sulfinic acids was prevented by their reported[2] low stability with respect to reagents and/or products an by the fact that ene and retro-ene reactions are comparatively easy. Actually, the recently reported[3] isolation of the stable sulfinic acid 5 from the ene reaction of th

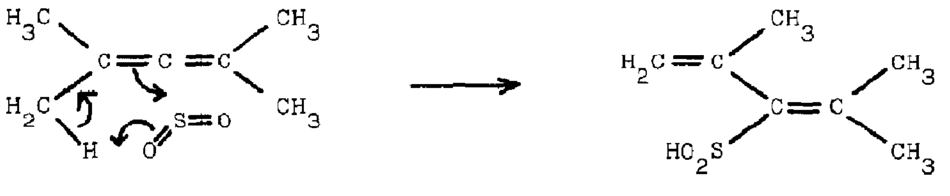


(2)

cyclic olefin 4 with sulfur dioxide (eq 2) is based on the circumstance that the pheny ring in 5 does not participate to the retro-ene reaction.

We wish to report here the observation and isolation of sulfinic acids, obtain from the ene addition of sulfur dioxide to methyl-substituted allenes, which also possess an "in se" stability with respect to the reagents. Other ene reactions of allenes have been reported.[4]

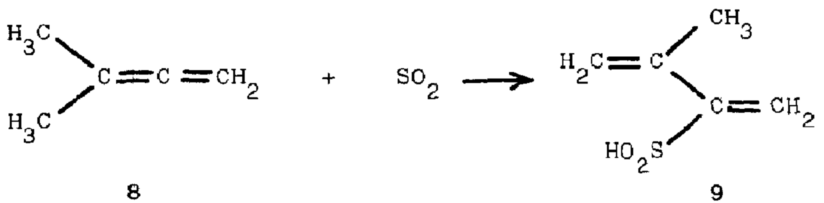
The ^1H nmr spectrum of tetramethylallene (2,4-dimethyl-2,3-pentadiene) 6 in CD shows a single resonance at 1.63 δ. The spectrum of the same compound in sulfur di at -60° is totally different, presenting three 3:3:3 methyl resonances (one of thes is a doublet of doublets) and two 1:1 multiplets in the vinyl proton region. This spectrum is consistent with the hypothesis of a complete conversion of 6 to the 3-(2,4-dimethyl-1,3-pentadienyl) sulfinic acid 7 (eq 3).



6 7 (

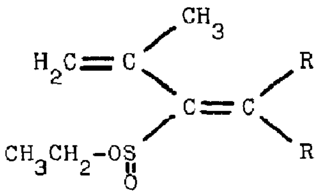
The ^{13}C nmr spectrum of 6 in sulfur dioxide is in agreement with the proposed structure, showing three different methyl resonances and four different resonances between 144 and 121 δ, which have to be attributed to the four vinylic carbons in 7. The magnetic parameters of sulfinic acid 7 are collected in the Table.

Differently from the tetramethyl-substituted substrate 6, the reaction of 3-methyl-1,2-butadiene 8 with sulfur dioxide is not istantaneous, having a half-tim of about 60 min at -10°. After completion only the ^1H and ^{13}C signals attributable the 2-(3-methyl-1,2-butadienyl) sulfinic acid 9 are observed (eq 4).



8 9 (4

The sulfinic acids 7 and 9 can be isolated by distillation of the solvent at - *in vacuo*. They decompose readily at room temperature and therefore, for the purpose further characterization, have been converted into the corresponding sulfinic ester 10 and 11 by reaction of their sodium salts with ethyl bromide in ethanol.[5] These esters easily rearrange to the isomeric sulfones 12 and 13, and actually only the sulfinic ester 10 could be isolated. Compounds 10, 12, and 13 gave satisfactory



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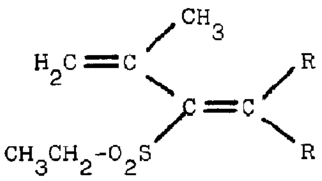
11 R = H

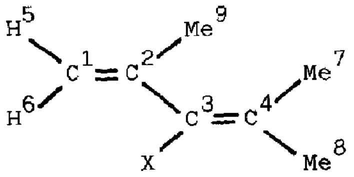


12 R = CH_3

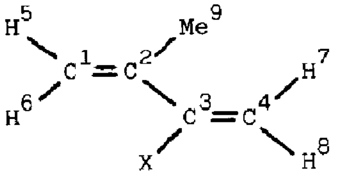
13 R = H

elemental analyses and correct ir and mass data;[6] their ^{1}H nmr parameters are shown in the Table.

Table. ^{1}H and ^{13}C nmr data for sulfinic acids 7 and 9 and for the corresponding ethyl sulfinic esters or sulfones 10, 12, and 13.



7, 10, 12



9, 13

^{1}H:

	X	Solv.	δ_5	δ_6	δ_7	δ_8	δ_9	$^2J_{56}$	$^2J_{78}$	$^4J_{59}$	$^4J_{69}$	$^5J_{57}$	$^5J_{58}$	$^5J_{67}$	$^5J_{68}$
7	HOSO	SO_2	5.39	4.89	1.86	2.07	1.93	2.2		1.5	1.1				
10	EtOSO–[a]	$CDCl_3$	5.34	4.86	1.84	2.03	1.93	2.1		1.6	1.0				
12	$EtSO_2$–[b]	$CDCl_3$	5.31	4.90	1.91	2.23	2.00	1.6		1.6	1.0				
9	HOSO	SO_2	5.33	5.44	5.91	6.05	2.01	0.3	1.3	1.5	0.7	0.5	1.2	0.6	0.5
13	$EtSO_2$–[c]	$CDCl_3$	5.33	5.68	6.00	6.37	2.04	1.1	0.4	2.0	0.7	0.4	1.0	0.4	0.5

[a] Ethyl resonances: diasterotopic methylene protons δ_{CH_2} 4.058 and δ'_{CH_2} 4.065; δ_{CH_3} 1.34; ^3J 6.9; $^3J'$ 7.2.

[b] Ethyl resonances: δ_{CH_2} 3.07; δ_{CH_3} 1.36; ^3J 7.5.

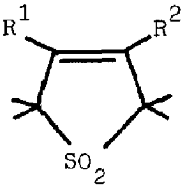
[c] Ethyl resonances: δ_{CH_2} 3.08; δ_{CH_3} 1.28; ^3J 7.3.

^{13}C:

	X	Solv.	δ_1	δ_2	δ_3	δ_4	δ_7	δ_8	δ_9
7	HOSO	SO_2	121.1	141.9	136.2	144.1	19.1	25.5	22.3
9	HOSO	SO_2	117.1	152.0	137.1	117.9			21.4

At variance with the behaviour of allenes 6 and 8, the spectrum of 1,2-butadi 14 in sulfur dioxide does not show any evidence for the conversion of 14 into the corresponding sulfinic acid, even after heating the solution at 80° for 48 h in a sealed tube; only the slow disappearance of the nmr signals of 14 and the formatio of an uncharacterizable precipitate is observed.

The stability of the sulfinic acids 7 and 9 is probably related to their conj gated dienylic structure, which does not easily allow the molecule to undergo the shift previously observed[1] nor the retro-ene reaction. It is noteworthy that, unde our reaction conditions, 7 and 9 show no tendency to further react with sulfur dio to give the cyclic adducts sulfolene 15 or δ-sultine 16.[7]



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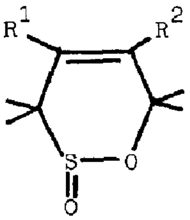

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R^1, R^2 = SO_2H or CH_3.

At the present stage of our research we cannot offer a rationale for the reac vity trend observed (6 > 8 >> 14). No comparative studies on the reactivity of vari substituted allenes in the ene reaction have insofar been made. We can only observ that the trend cannot be related to statistical factors only, but that the enhance nucleophilicity of allenes upon methyl substitution should also be considered.

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[6] Oily material purified by column chromatography. ir (liquid film), $\nu_{S=O}$, 10: 1132; 12: 1305 and 1 13: 1300 and 1110 cm^{-1}. Anal., 10: C 55.95, H 7.9; 12: C 54.05; H 7.85; calc. for $C_9H_{16}O_2S$: C 57. H 8.56; 13: C 52.45, H 7.3; calc. for $C_7H_{12}O_2S$: C 52.47, H 7.55.

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