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SYNTHESES OF VINYL SULFONATES VIA "SULFENE" INTERMEDIATES*

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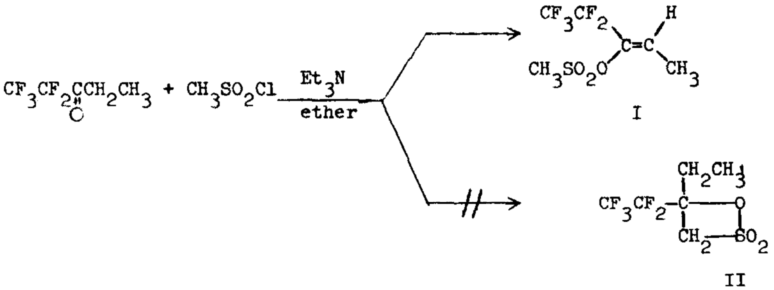
In our previous communication[1] we reported that certain perhalogenated ketones and aldehydes yielded β-sultones when they were treated with alkanesulfonyl chlorides in the presence of triethylamine. Recent interest in sulfene reactions[2] and vinyl (enol) sulfonate syntheses[3,4] prompts us to report our results with halogenated ketones and aldehydes containing one or more α-hydrogens. Unlike their perhalogenated analogs, these ketones and aldehydes gave vinyl sulfonates under comparable conditions. For example, treatment of an ethereal solution of perfluoroethyl ethyl ketone and methanesulfonyl chloride with an equivalent amount of triethylamine in the same solvent at -10° (± 2°) under nitrogen gave 81% of pure 4,4,5,5,5-pentafluoropent-2-en-3-yl methanesulfonate. Further examples are listed in Table I.



Structure I was proven on the basis of elemental analyses, molecular weight determination, and spectral data. In addition to the C=C (5.9 μ) and SO_2 (7.24 and 8.4 μ) absorptions in its

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*Based partly on Lilian Kao Liu's Ph.D. Thesis, Purdue University, June, 1969.

TABLE I

Vinyl Sulfonates from Various Carbonyl Compounds

Vinyl Sulfonate[a]	bp° (mm)	mp (°C)	$N^{20}D$	Isolation yield (%)
$CH_3SO_3(CF_3CF_2)C{=}CHCH_3$	64° (0.2)	-	1.3805	81
$CH_3SO_3(CF_3)C{=}CH_2$	26° (0.2)[b]	-	1.3820[b]	74
$C_6H_5CH_2SO_3(CF_3)C{=}CH_2$	-	58-59.5°	-	22
$CH_3SO_3(CCl_3)C{=}CH_2$	72° (0.1)[c]	37-38°[c]	-	52[d]
$CH_3SO_3(CH_2Cl)C{=}CHCl$	91° (0.2)	-	1.4983	66
$CH_3SO_3(CH_3)C{=}CCl_2$	66° (0.1)	-	1.4867	33
$CH_3SO_3(CHCl_2)C{=}CCl_2$	97° (0.1)	-	1.5280	30
$CH_3SO_3(C_6H_5)C{=}CCl_2$	119° (0.05)	-	1.5660	31
$CH_3SO_3CH{=}CCl_2$	e	-	1.4855	10

[a] Satisfactory elemental analyses and molecular weights were obtained for all new compounds. All melting points and boiling points are uncorrected.

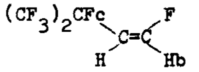
[b] Lit.[2] bp 54° (4.5), $N^{20}D$, 1.3806

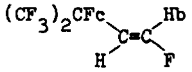
[c] Lit.[2] bp 82° (0.2), mp 37-38°

[d] Obtained by addition of methanesulfonyl chloride to a mixture of ketone and amine.

[e] Isolated by vpc using a 8' 10% SF-96 column (on chromosorb G) at 140°.

ir spectrum, the mass spectrum showed a molecular ion (m/e = 254) with m/e = 79 ($CH_3\overset{+}{S}O_2$) as the most abundant ion. Its nmr spectrum consisted of one singlet at δ 3.21 (3H, $\underline{CH_3}SO_2$), two triplets at 1.89 and 2.01 (3H, $\underline{CH_3}C{=}C$, $J_{CH_3-H}=7Hz$, $J_{CH_3-CF_2}=2.5Hz$), and a quartet at 6.38 (1H, olefinic H, $J_{CH_3-H}=7Hz$). Both the splitting pattern and the integration values were in excellent agreement with the assigned structure. Several F-F and H-F spin coupling constants have been measured in cis- and trans-1-fluoro-2-(perfluoroisopropyl) ethylenes.[5] The coupling constant between Fc and Hb in the cis- and trans- isomers were 2.1 and about 0.0 Hz, respectively.





J_{HbFc} 2.1 Hz ~0.0 Hz

The fact that the coupling constant between CF_2 and the olefinic proton is about zero strongly suggests that the olefinic proton is cis to the perfluoroethyl group as indicated in structure I. Structures of the other vinyl sulfonates were assigned on the basis of like data.

1,1,1-Trichloroacetone gave a considerably lower yield (20-25%) of the corresponding vinyl sulfonate under similar conditions, but the yield was greatly improved (52%) by addition of an ethereal solution of methanesulfonyl chloride to a mixture of triethylamine and the ketone at 0°. The product could be isolated easily by removal of the unchanged 1,1,1-trichloroacetone under vacuum at room temperature followed by recrystallization of the residual oil in a mixture of carbon tetrachloride and n-hexane. This procedure avoided the decomposition encountered in the distillation.

The vinyl sulfonate skeleton was further proven by chemical degradation. For example, treatment of an ethereal solution of 3,3,3-trichloropropen-2-yl methanesulfonate with 10% excess 0.5 N sodium hydroxide at room temperature for 24 hr led to 37% recovery of the vinyl sulfonate together with a mixture of water soluble sodium salts. When the sodium salts were treated with aqueous S-benzylthiuronium chloride, S-benzylthiuronium acetate and methanesulfonate were isolated by fractional recrystallization, and were identified by comparison of the infra red spectra and mixed melting points with authentic samples. The formation of the acetate ion can easily be explained by S-O cleavage with regeneration of the carbonyl compound,[4] followed by a haloform cleavage to give chloroform and sodium acetate.

Among the known vinyl sulfonate syntheses which are suitable for laboratory preparations, Peterson's procedure,[3] which works well with vinyl tosylates, cannot be applied to the methanesulfonates since potassium t-butoxide is known to give mainly cleavage products.[6] Also the procedure of Mazur and co-workers[4] suffers from the easy decomposition of the methanesulfonic anhydride; and no appreciable vinyl sulfonate could be isolated when 1,1,1-trichloroacetone was heated under reflux with 1.5 equivalents of methanesulfonic anhydride in dimethylformamide for 2 hr. The present procedure appears to be the simplest method for preparation of halogen-substituted vinyl sulfonates and is generally applicable to aliphatic as well as aromatic halogenated ketones containing one or more α-hydrogens.

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