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MICHAEL ADDITIONS TO TRIFLUOROMETHYLVINYL SULFONE

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SUMMARY

Michael addition reactions of trifluoromethyl vinyl sulfone with organic compounds with labile hydrogen atoms are studied. Such additions can be successfully accomplished using potassium fluoride and 18-crown-6-ether or benzyltrimethylammonium hydroxide (Triton B) as catalysts.

INTRODUCTION

A strongly polarized double bond in trifluoromethyl vinyl sulfone is the cause of the high reactivity of this compound and makes it an interesting object for investigation. The properties of two other ethylenes with strongly polarized double bonds - propenylnitrile and nitroethene - are well studied, but very few publications are directed to the chemistry of trifluoromethyl vinyl sulfone [1 - 3].

RESULTS AND DISCUSSION

This paper presents the results of our study of the interaction of trifluoromethyl vinyl sulfone with organic compounds, possessing labile hydrogen atoms in methylene and methyl groups. Up to now the only known example of such a reaction is the addition of malonic ester to trifluoromethyl vinyl sulfone catalyzed by sodium [2].

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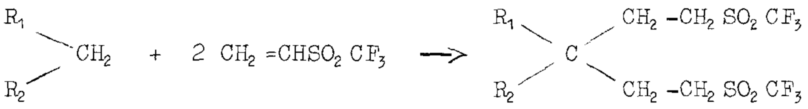
But, we have found that the application of metallic sodium for the catalysis of such a Michael addition in the case of trifluoromethyl vinyl sulfone often requires a tedious search for the proper reaction conditions. Slight deviations from the optimum lead to an increase in rate of the concurrent oligomerisation of trifluoromethyl vinyl sulfone. A fast oligomerisation of this olefin is also often observed when triethylamine is used as the catalyst for the addition. The use of the usual catalysts of the cyanethylation reaction - sodium hydroxide or sodium methylate - is hindered by the low stability of the CF_3SO_2 group in such reaction media.

We wish now to report that KF in aprotic solvents containing 18-crown-6-ether earlier shown to be an efficient and powerful catalyst for Michael additions to propenylnitrile [4], can be successfully applied also for the catalysis of the addition of organic compounds possessing labile hydrogen atoms in methylene and methyl groups to trifluoromethyl vinyl sulfone. High yields (up to 90%) of Michael addition products can be obtained in acetonitrile after 1.5-2 hour stirring of the reaction mixture, see e.g. compound (2a). The yields in benzene and CH_2Cl_2 are a little lower (table 1, method A)



(1a - 1e) (2a - 2e)

	a	b	c	d	e
R_1 =	CH_3CO-	C_2H_5OOC-	CH_3CO-	C_6H_5CO-	NC-
R_2 =	CH_3CO-	C_2H_5OOC-	C_2H_5OOC-	C_2H_5OOC-	NC-

We have also shown that Michael addition of compounds (1a - 1e) to trifluoromethyl vinyl sulfone can be successfully accomplished when a 40% methanol solution of benzyltrimethylammonium hydroxide (Triton B) is used as a catalyst. The addition goes smoothly to about 70% yield when $CF_3SO_2CH=CH_2$ is dropped into the solution of compounds (1a - 1e) in dioxane (table 1, method B).

TABLE 1

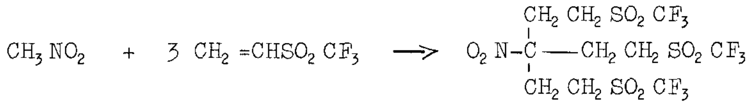
Michael additions of compounds 1a-e and CH_3NO_2 to trifluoromethyl vinyl sulfone

Starting compound	Method	Solvent	Reaction time	Adduct	(yield) %
Ia	A	CH_3CN	1	2a	(68)
		-"-	1.5		(87)
		-"-	2		(89)
		CH_2Cl_2	1.5		(69)
		-"-	2		(73)
		C_6H_6	1.5		(58)
		-"-	2		(64)
	B	dioxane	12	2a	(74)
Ib	A	CH_3CN	2	2a	(91)
		CH_2Cl_2	1.5		(75)
		C_6H_6	1.5		(68)
	B	dioxane	12	2b	(73)
Ic	A	CH_3CN	2	2c	(87)
		CH_2Cl_2	2		(76)
		C_6H_6	2		(71)
	B	dioxane	12	2c	(68)
Id	A	CH_3CN	1.5	2d	(88)
		CH_2Cl_2	2		(75)
		C_6H_6	2		(73)
	B	dioxane	12	2d	(70)
Ie	A	CH_3CN	1.5	2e	(86)
		CH_2Cl_2	1.5		(69)
		C_6H_6	1.5		(71)
	B	dioxane	12	2e	(68)
CH_3NO_2	A	CH_3CN	2	3	(85)
		CH_2Cl_2	1.5		(71)
		C_6H_6	1.5		(64)
	B	dioxane	12	3	(67)

Both these catalysts, however, failed to promote the addition of ethyl α-(trifluoromethylthio)acetoacetate to trifluoromethyl vinyl sulfone. Only the initial CF_3S-substituted ethyl acetoacetate and resinous products of the oligomerisation of trifluoromethyl vinyl sulfone were recovered from the reaction mixtures. A possible explanation of this fact is the extremely high degree of acidity of the hydrogen atom adjacent to the CF_3S group, by which ethyl α-(trifluoromethylthio)acetoacetate exists primarily in the enol form. It has earlier been shown that for the reaction to occur it is essential that the reaction mixture be alkaline to moist litmus [5].

The powerful electronegative inductive effect of the CF_3SO_2 group seems to lead to an increase in the lability of the second hydrogen atom of the methylene group after the addition of compounds (1a - 1e) to the first molecule of trifluoromethyl vinyl sulfone. Even with a molar ratio of compounds (1a - 1e) to $CF_3SO_2CH{=}CH_2$ of 10:1 only the products of double addition (yields up to 80% with respect to $CF_3SO_2CH{=}CH_2$) were isolated.

Likewise trifluoromethyl vinyl sulfone combines with nitromethane to give, under similar conditions, the product of trisaddition as the sole product, though the molar ratio of nitromethane to $CF_3SO_2CH{=}CH_2$ was changed from 1:3 to 20:1



$$CH_3NO_2 \quad + \quad 3\ CH_2{=}CHSO_2CF_3 \quad \longrightarrow \quad O_2N{-}\underset{\displaystyle CH_2CH_2SO_2CF_3}{\overset{\displaystyle CH_2CH_2SO_2CF_3}{C}}{-\!\!-}CH_2CH_2SO_2CF_3$$

(3)

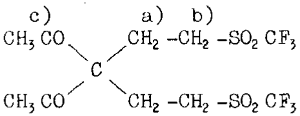
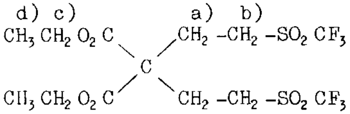
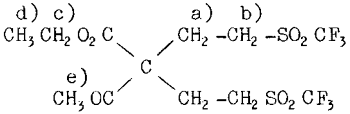
It is interesting to note that propenylnitrile under the same conditions gives either mono- or as of trisadditionproducts.

EXPERIMENTAL

All the reagents were available commercially, except trifluoromethyl vinyl sulfone, which was prepared according to [1]. The analytical data and physical properties of new compounds are shown in table 2. NMR ^{19}F spectra were recorded in C_6F_6 solution, using the solvent as an internal standard on a Bruker HX-60 spectrometer. ^1H NMR spectra of compounds (2a - 2d) were re-

TABLE 2

Analytical and characteristic data of adducts

Compound	m.p.°C (solvent)	C,% Found (cal.)	H,% Found (cal.)	^{19}F-NMR	^{1}H-NMR	IR, cm^{-1}
 (2a)	94 (ethanol)	31.50 (31.43)	3.35 (3.33)	78.1	a) 3.2(m) b) 2.5(m) c) 2.3(s)	2990(m), 2940(m), 1730(vs), 1695(vs) 1480(m), 1365(vs), 1345(vs), 1275(vs) 1225(vs), 1120(vs), 1050(m), 960(m), 785(m), 725(s), 690(s),640(m), 610(m), 540(m), 500(s),
 2b)	67-68 [2] (ethanol)			78.4	a) 3.4(m) b) 2.4(m) c) 4.2(q) d) 1.3(t)	2980(m), 2930(m), 1745(s), 1725(s), 1370(m,b), 1125(m), 1015(s), 860(m), 780(m), 740 (s), 620 (vs), 535 (m), 485 (s)
 (2c)	50-51 (ethanol/ H_2O)	31.87 (32.07)	3.71 (3.56)	78.8	a) 3.3(m) b) 2.4(m) c) 4.3(q) d) 1.3(t) e) 2.2(s)	2980(m), 1740(s), 1715(vs), 1375(vs) 1220(s,b), 1120 (vs), 1115(m), 775(m), 740(m), 595(m), 535(m), 450(m)

corded in $CDCl_3$ and of compounds (2e, 3) in CD_3CN on a Bruker WP-80 spectrometer with TMS as an internal standard in all cases. ^1H and ^{19}F chemical shifts are expressed in ppm upfield from internal TMS or CCl_3F, respectively. The NMR spectra confirm the proposed structures of the adducts (2, 3). The fine ^1H structure of the two methylene groups in $CF_3SO_2CH_2CH_2-$ is, however, more complicated than simple triplets, perhaps because of the coupling with fluorine atoms of CF_3SO_2 group. I.r. spectra were recorded as KBr disks using a Perkin-Elmer model 457 spectrometer.

Addition of organic compounds possessing labile hydrogen atoms to trifluoromethyl vinyl sulfone

Method A. To a solution of 18-crown-6-ether (0.01 mmol) in appropriate water free solvent (20 ml) dry KF (ca. 0.3 mmol) was added followed by compound (1a - 1e) or CH_3NO_2 (3 mmol) and trifluoromethyl vinyl sulfone (6 mmol). The mixture was stirred at 80°C for 1.5 - 2 h. Solvent was removed in vacuo, CH_2Cl_2 was added and the organic layer was washed with 2M HCl. Removal of the solvent leaves a solid or a slowly crystallized oil, which is purified by recrystallization.

Method B. To a solution of compound (1a - 1e) or CH_3NO_2 (5 mmol) and a 40% methanol solution of benzyltrimethylammonium hydroxide (Triton B) (0.5 mmol) in dry dioxane (5 ml) a solution of trifluoromethyl vinyl sulfone (4.9 mmol) in dry dioxane (3 ml) was added dropwise under stirring at 20-25°C. The reaction mixture was stirred under the same conditions for 12 h, poured onto ice, extracted with CH_2Cl_2, washed with water and dried with $MgSO_4$. Work-up was similar to method A.

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