

RADICAL ADDITION REACTIONS ON 1,1-DIFLUORO-1-OLEFINS

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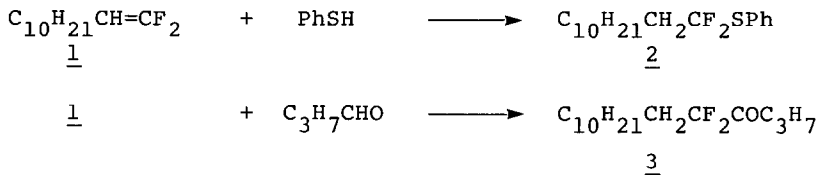
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Radical addition reactions on 1,1-difluoro-1-olefins produced adducts having attacking radical species on the terminal carbon.

Free radical chain addition to carbon-carbon double bond is an important synthetic method of wide scope. As for fluorinated olefins, reactivity of a variety of radical species toward polyfluorinated ethenes and propenes has been examined so far.^{1),2)} For unsymmetrical fluoroethenes, two possible addition products have been produced and the orientation ratios (O_r) of various radicals have been determined.²⁾ In order to know the effect of alkyl and aryl substitution on the orientation of radical additions to fluorinated olefins, we subjected some 1,1-difluoro-1-olefins to radical addition reactions, the results being reported in this communication.

When 1,1-difluoro-1-dodecene 1 was heated with thiophenol in tetrahydrofuran in the presence of a small amount of benzoyl peroxide, an adduct 2³⁾ was isolated in 49% yield after chromatographic purification. The ¹⁹F-NMR spectrum of the crude reaction mixture showed no absorption for the other expected 1:1 adduct. Similarly, addition of butyraldehyde on 1, induced by peroxide, gave 3⁴⁾ in 34% yield as the sole isolable product. Results for other fluoroolefins are summarized in Table. The results clearly tell that in all cases initial attack of radical intermediate occurred on the terminal fluorine-carrying carbon. This would indicate that fluorine substituent destabilizes the formation of radical center on the same carbon.



Table; Radical addition on 1,1-difluoro-1-olefins.

olefin	reagent	product	yield(%)
$C_{10}H_{21}CH=CF_2$ <u>1</u>	PhSH	$C_{10}H_{21}CH_2CF_2SPh$ <u>2</u>	58
"	C_3H_7CHO	$C_{10}H_{21}CH_2CF_2COC_3H_7$ <u>3</u>	34
$p-H_3C-C_6H_4-CH=CF_2$	PhSH	$p-H_3C-C_6H_4-CH_2CF_2SPh$	78
$p-NC-C_6H_4-CH=CF_2$	PhSH	$p-NC-C_6H_4-CH_2CF_2SPh$	74
$p-Cl-C_6H_4-CH=CF_2$	PhSH	$p-Cl-C_6H_4-CH_2CF_2SPh$	49
"	$HSCH_2CO_2Et$	$p-Cl-C_6H_4-CH_2CF_2SCH_2CO_2Et$	69
"	C_3H_7CHO	$p-Cl-C_6H_4-CH_2CF_2COC_3H_7$	8

Reaction of 1 with carbon tetrachloride gave a complex mixture of products, from which no identifiable product was obtained. This would be due to the high reactivity of initially formed 1:1 adduct under the reaction conditions. Present method may be useful for the syntheses of unique fluorine-containing functional groups.

REFERENCES AND NOTES

- 1) R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, **1956**, 61; J. M. Tedder, J. C. Walton, and K. D. R. Winton, *J. Chem. Soc., Faraday I*, **68**, 1866 (1972).
- 2) J. M. Tedder and J. C. Walton, *Accounts Chem. Res.*, **9**, 183(1976).
- 3) $^1H-NMR(CDCl_3)$ 0.86(3H), 1.2-1.7(18H), 1.9-2.3(2H), 7.2-7.4(3H), 7.5-7.65(2H); $^{19}F-NMR(CDCl_3)$ (downfield in ppm from external CF_3CO_2H) +6.3(t, J=15Hz); MS m/e 315(M^++1 , 2%), 314(M^+ , 10%).
- 4) $^1H-NMR(CDCl_3)$ 0.88(3H), 0.95(3H), 1.2-2.0(22H), 2.62(2H); $^{19}F-NMR(CDCl_3)$ -28.4(t, J=17Hz); correct elemental analysis.

(Received in Japan 7 March 1981)