Tetrahedron Letters No. 13, pp 1009 - 1012, 1976. Pergamon Press. Printed in Great Britain.

ELECTROPHILIC SUBSTITUTIONS OF OLEFINIC HYDROGENS I.

ACYLATION OF VINYL SULFIDES

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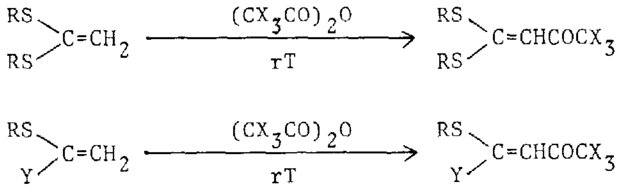
(Received in Japan 8 January 1976; received in UK for publication 17 February 1976)

In the course of our investigation on the chemistry of trithioorthoacetates $(ArS)_3C\text{-}CH_3$, it was found that these compounds react with trifluoroacetic anhydride quite easily at room temperature, giving $(ArS)_2C{=}CHCOCF_3$ in almost quantitative yields[1]. The products were seemed to be resulted from electrophilic attack of the acid anhydride on ketene dithioacetals $(ArS)_2C{=}CH_2$, probably formed by an acid-catalyzed elimination of ArSH from the trithioorthoacetates. This reasoning prompted us to investigate, develop and generalize a reaction, an electrophilic substitution of olefinic hydrogens in fair yields, starting first with ketene dithioacetals and then with various kinds of vinyl sulfides. Expectedly, trifluoroacetylation and trichloroacetylation occurred quite easily at room temperature to give corresponding acylated olefins in high yields, and we now wish to communicate these results (Table I).



$$(RS)_2C{=}CH_2 \xrightarrow[rT]{(CX_3CO)_2O} (RS)_2C{=}CHCOCX_3$$

$$(RS)(Y)C{=}CH_2 \xrightarrow[rT]{(CX_3CO)_2O} (RS)(Y)C{=}CHCOCX_3$$

(R=aryl, alkyl; Y=H, aryl; X=F, Cl)

In a typical experiment, to a stirred mixture of ketene dithioacetal $(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CH_2$[2] (0.650 g, 2.4 mmol) and a small amount of pyridine (0.128 g) in 3 ml of $CHCl_3$ was added 0.688 g (3.3 mmol) of trifluoroacetic anhydride and allowed to stand for 14 hr at room temperature, which gave after usual workup 0.816 g (93 % yield) of $(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCOCF_3$, mp 166°[1]. Inspection of the nmr spectrum for the reaction mixture showed that this reaction proceeded cleanly without formation of any detectable amounts of by-products. In the absence of pyridine, however, much resinous products were formed[3]. Reaction of $(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CH_2$ with CCl_3COCl or its acid anhydride gave $(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCO\text{-}CCl_3$, mp 145°[1], in 98 % and 96 % yields, respectively. Similarly, reaction with $ClCH_2COCl$ afforded $(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCOCH_2Cl$, mp 153°[1], in 59 % yield.

Table I

Acylation of Ketene Dithioacetals and Vinyl Sulfides

Reactants	Acylating Reagents	Products	Yields(%)
$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CH_2$	$(CF_3CO)_2O$	$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCOCF_3$	93
$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CH_2$	$(CCl_3CO)_2O$	$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCOCCl_3$	96
$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CH_2$	CCl_3COCl	$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCOCCl_3$	98
$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CH_2$	$ClCH_2COCl$	$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCOCH_2Cl$	59
$\underline{p}\text{-}ClC_6H_4SCH{=}CH_2$	$(CF_3CO)_2O$	$\underline{p}\text{-}ClC_6H_4SCH{=}CHCOCF_3$ [a]	97
$\underline{p}\text{-}ClC_6H_4SCH{=}CH_2$	CCl_3COCl	$\underline{p}\text{-}ClC_6H_4SCH{=}CHCOCCl_3$ [b]	91
$CH_3SCH{=}CH_2$	$(CF_3CO)_2O$	$CH_3SCH{=}CHCOCF_3$ [c]	100
$C_6H_5S\cdot C_6H_5C{=}CH_2$	$(CF_3CO)_2O$	$C_6H_5S\cdot C_6H_5C{=}CHCOCF_3$ [c]	79
$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CH_2$	$CF_3COOCOCH_3$	$(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCOCF_3$	40

[a] an equimolar mixture of *cis* and *trans* isomers. [b] the *cis* isomer.
[c] mixtures of *E* and *Z* isomers.

This substitution reaction can be applicable to vinyl sulfides. For instance reaction of *p*-chlorophenyl vinyl sulfide with trifluoroacetic anhydride at room temperature gave 97 % yield of $\underline{p}\text{-}ClC_6H_4SCH{=}CHCOCF_3$, the nmr spectrum of which showed to be an almost equimolar mixture of the *cis*- and *trans*-isomers. Recrystallization from benzene-*n*-hexane yielded pure *cis*-isomer[4]: mp 118°; nmr ($CDCl_3$)[5] δ 7.39 (s, 4, ar.), 7.71 (d, 1, J=10.2 Hz), 6.60 (d, 1, J=10.2 Hz); *Anal*. Calcd. for $C_9H_6ClF_3OS$: C,45.04; H,2.27; Cl,13.30; F,21.37; Found: C,45.34; H,2.45; Cl,13.37; F,21.09. Trichloroacetylation (in chlorobenzene at 100° for 2 days) afforded *cis*-$\underline{p}\text{-}ClC_6H_4SCH{=}CHCOCCl_3$[6], mp 121°, in 91 % yield.

Methyl vinyl sulfide and phenyl α-styryl sulfide were also trifluoroacetylated easily at room temperature in 100 % and 79 % yields (before separation of the isomers), respectively.

Formally, this reaction resembles acylation of enamines[7]. However, it appears that there exist some differences in nature between these two reactions. Although iminium ions are usually isolable in the case of acylation of enamines, no indication implying intermediacy of such a species was observed in this reaction, at least in some runs followed carefully by nmr. In contrast to the case of enamines, neither acetyl chloride nor acetic anhydride reacted with vinyl sulfides and with ketene dithioacetals[8]. In connection to these facts, it seems of much interest to note that a mixed anhydride $CH_3COOCOCF_3$, which is a stronger acylating reagent than acetic anhydride and by which ordinarily acetylation (not trifluoroacetylation) occurs[9,10], was found to react easily with ketene dithioacetals but the reaction actually occurred was trifluoroacetylation and not acetylation. For instance, reaction of $(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CH_2$ with the mixed anhydride gave $(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCOCF_3$[1] in 40.4 % yield as a sole identifiable product, no $(\underline{p}\text{-}CH_3C_6H_4S)_2C{=}CHCOCH_3$ being detected. Another feature of this reaction can be seen in the effects of β-substituents. Although acylation of enamines[7] and acid-catalyzed hydrolysis of vinyl sulfides[12] proceed without much difficulty in the presence of β-substituents, acylation of vinyl sulfides is completely inhibited by the presence of β-substituents. For example, phenyl propenyl sulfide did not react with trifluoroacetic anhydride even at elevated temperatures, the starting material being recovered unchanged. Extention of the present reaction is now undertaken in our laboratory, together with some experiments from mechanistic standpoint of view.

REFERENCES AND NOTES

1. M. Hojo and R. Masuda, J. Org. Chem., **40**, 963 (1975).
2. Prepared according to the method of W. E. Truce and R. J. Steltenkamp [J. Org. Chem., **27**, 2816 (1962)].

3. In contrast, reaction of trithioorthoacetates with trifluoroacetic anhydride doesn't occur in the presence of pyridine[1].

4. The *trans* isomer obtained is an oil and not analytically pure yet; nmr ($CDCl_3$) δ 8.24 (d, 1, *J*=15.0 Hz), 7.25 (s, 4, ar.), 6.21 (d, 1, *J*=15.0 Hz).

5. Recorded on an nmr spectrometer, Hitachi R-24.

6. All new compounds gave satisfactory elemental analyses (C, H, F or C, H, S, Cl) and showed nmr spectra consistent with the proposed structures.

7. For a review, see A. G. Cook, Ed., " *Enamines: Synthesis, Structure and Reactions* ", Marcel Dekker, New York, 1969.

8. In the presence of pyridine no reaction occurred and in the absence of pyridine much resinous materials were produced by prolonged heating.

9. For a review, see L. F. Fieser and M. Fieser, " *Reagents for Organic Synthesis* ", John Wiley and Sons, Inc., New York, 1967, *p* 1222.

10. The mixed anhydride is reported[11] to react with simple olefins to give addition products, from which trifluoroacetic acid is eliminated by refluxing in methanol to yield acetylated olefins.

11. A. L. Henne and J. M. Tedder, *J. Chem. Soc.*, 3628 (1953).

12. Private communication from Profs. T. Fueno and T. Okuyama.