

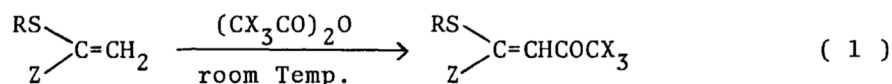
ELECTROPHILIC SUBSTITUTIONS OF OLEFINIC HYDROGENS II.
ACYLATION OF VINYL ETHERS AND N-VINYL AMIDES

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Reactions of vinyl ethers, N-vinyl carboxamides and N-vinyl sulfonamides with trifluoroacetic (or trichloroacetic) anhydride occurred quite easily at room temperature to give corresponding β -trifluoro- or trichloroacetylated compounds in high yields. Reactions with a mixed anhydride, $\text{CH}_3\text{COOCOCF}_3$, gave trifluoroacetylated compounds in high yields, acetyl compounds being not produced.

In our preceding communication¹ it was reported that ketene dithioacetals and vinyl sulfides react with trifluoroacetic anhydride quite easily at room temperature to give corresponding β -trifluoroacetylated compounds in high yields. As an extension of this work we have tried trifluoro- and trichloroacetylation of



(R=aryl, alkyl; Z=aryl, alkyl, arylthio; X=F, Cl)

vinyl ethers, N-vinyl sulfonamides and N-vinyl carboxamides. As anticipated



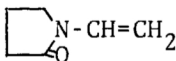
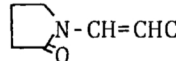
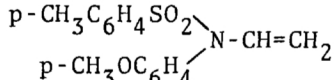
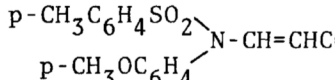
(R=aryl, alkyl; Y= -O-, -SO₂N-, -CON-; X=F, Cl)

these reactions did proceed quite easily at room temperature to afford corresponding β -acylated products in high yields. Having been thus established that these electrophilic substitution reactions of olefinic hydrogens are general not only for vinyl sulfides but also for vinyl ethers and vinyl amides, we now wish to communicate these results (Table I).

In a typical experiment, to a stirred mixture of ethyl vinyl ether (2.2 g, 30 mmol) and pyridine (0.8 g, 10 mmol) in dichloromethane (18 g) was added

dropwise 9.0 g (43 mmol) of trifluoroacetic anhydride at room temperature and the solution was allowed to stand overnight. After usual work-up there was obtained a quantitative yield (5.1 g) of trans-C₂H₅OCH=CHCOCF₃: bp 51°C/12 mmHg; nmr (δ , CDCl₃): 7.90 (d, 1H, J=11.4 Hz), 5.85 (d, 1H, J=11.4 Hz), 4.15 (t, 3H); ir (KRS-5, cm⁻¹): ν_{CO} 1705, $\nu_{\text{C=C}}$ 1590; Anal: Calcd for C₆H₇O₂F₃: C, 42.87; H, 4.20; F, 33.90; Found: C, 43.09; H, 4.35; F, 33.70. Trichloroacetylation of ethyl vinyl ether with trichloroacetic anhydride gave trans-C₂H₅OCH=CHCOCCl₃² in 71 % yield. Similarly, trifluoro- and trichloroacetylation of ethyl α -p-nitrophenylvinyl ether occurred easily, giving quantitative yields of C₂H₅O(p-O₂N-C₆H₄)C=CHCOCF₃^{2,3}, mp 79°C, and C₂H₅O(p-O₂NC₆H₄)C=CHCOCCl₃^{2,3}, mp 109°C, respectively.

Table I
Acylation of Vinyl Ethers and N-Vinyl Amides

Reactants	Acyating Reagents	Products	Yield(%)
C ₂ H ₅ OCH=CH ₂	(CF ₃ CO) ₂ O	C ₂ H ₅ OCH=CHCOCF ₃ ^a	100
C ₂ H ₅ OCH=CH ₂	(CCl ₃ CO) ₂ O	C ₂ H ₅ OCH=CHCOCCl ₃ ^a	71
C ₂ H ₅ O(p-O ₂ NC ₆ H ₄)C=CH ₂	(CF ₃ CO) ₂ O	C ₂ H ₅ O(p-O ₂ NC ₆ H ₄)C=CHCOCF ₃ ^b	100
C ₂ H ₅ O(p-O ₂ NC ₆ H ₄)C=CH ₂	(CCl ₃ CO) ₂ O	C ₂ H ₅ O(p-O ₂ NC ₆ H ₄)C=CHCOCCl ₃ ^b	100
p-CH ₃ C ₆ H ₄ SO ₂ N(Ph)CH=CH ₂	(CF ₃ CO) ₂ O	p-CH ₃ C ₆ H ₄ SO ₂ N(Ph)CH=CHCOCF ₃ ^a	92
p-CH ₃ C ₆ H ₄ SO ₂ N(Ph)CH=CH ₂	(CCl ₃ CO) ₂ O ^c	p-CH ₃ C ₆ H ₄ SO ₂ N(Ph)CH=CHCOCCl ₃ ^a	54
CH ₃ SO ₂ N(Ph)CH=CH ₂	(CF ₃ CO) ₂ O	CH ₃ SO ₂ N(Ph)CH=CHCOCF ₃ ^a	95
CH ₃ SO ₂ N(Ph)CH=CH ₂	(CCl ₃ CO) ₂ O ^c	CH ₃ SO ₂ N(Ph)CH=CHCOCCl ₃ ^a	94
 N-CH=CH ₂	(CF ₃ CO) ₂ O	 N-CH=CHCOCF ₃ ^a	56
 N-CH=CH ₂	CH ₃ COOCOCF ₃	 N-CH=CHCOCF ₃ ^a	100

^a trans isomers ^b not determined yet as to geometrical isomerism
^c Trichloroacetyl chloride can also be used.

N-Vinyl-p-toluenesulfonamide was also trifluoroacetylated to give trans-p-CH₃C₆H₄SO₂N(Ph)CH=CHCOCF₃, in 92 % yield: mp 99-100°C; nmr (δ , CDCl₃): 8.66 (d, 1H, J=13.2 Hz), 7.60-6.84 (m, 9H), 5.15 (d, 1H, J=13.2 Hz), 2.45 (s, 3H); ir (KBr, cm⁻¹): ν_{CO} 1706, $\nu_{\text{C=C}}$ 1580, ν_{SO_2} 1327, 1169; Anal: Calcd for

$C_{18}H_{12}F_3SO_2$: C, 55.28; H, 3.82; F, 15.43: Found: C, 55.64; H, 3.89; F, 15.35. The trichloroacetyl derivative, trans- p - $CH_3C_6H_4SO_2N(Ph)CH=CHCOCCl_3$ ², mp 145°C, was obtained in 54 % yield. Starting with *N*-vinylmethanesulfonamide trifluoro- and trichloroacetylation gave trans- $CH_3SO_2N(Ph)CH=CHCOCF_3$ ², mp 159°C, and trans- $CH_3SO_2N(Ph)CH=CHCOCCl_3$ ², mp 170°C, in 95 and 94 % yields, respectively.

This reaction can also be applicable to *N*-carboxamides. For example, reaction of *N*-vinylpyrrolidone with $(CF_3CO)_2O$ at room temperature for 4 hr gave trans-*N*- β -trifluoroacetylvinylpyrrolidone², mp 96-97°C, in 56 % yield.

Interestingly, all these vinyl ethers and vinyl amides gave exclusively trans acylated isomers, in contrast to the case of vinyl sulfides¹, where mixtures of cis and trans isomers were invariable products. Neither acetic anhydride nor acetyl chloride reacted with vinyl ethers and vinyl amides, as was the case of vinyl sulfides¹.

Olefinic compounds have long been characterized by the electrophilic addition reactions in contrast to the electrophilic substitution reactions for aromatic compounds. In fact many kinds of reactions reported so far for vinyl sulfides, vinyl ethers and vinyl amides, which are susceptible to attack by electrophilic reagents, are all addition reactions⁴. It is not certain at present why trifluoro- and trichloroacetic anhydrides alone can give substitution products in high yields without formation of any addition products. Most likely, powerful electron-attracting ability of $COCF_3$ (or $COCCl_3$) group would be responsible for it; a possible intermediate (or transition state) for the present reaction, $-Y-\overset{\ddagger}{C}H-CH_2COCF_3$ ($Y = -S-, -O-, -SO_2N-, -CON-$), would choose deprotonation to give substitution products rather than collapsing with nucleophiles to give addition products. In the case of acetylation of enamines⁵, the corresponding species are stable iminium ions, $>\overset{\ddagger}{N}=CH-CH_2COCH_3$, and are isolable⁶. Regarding this view, it seems of interest to note here that vinyl ethers and vinyl amides as well as vinyl sulfides¹ can react with a mixed anhydride $CH_3COOCOCH_3$ to give trifluoroacetylated compounds instead of acetylated compounds^{7,8}. For example, reaction of *N*-vinyl-*p*-toluenesulfon-*p*-anisidide with this mixed anhydride gave almost quantitative yield of trans- p - $CH_3C_6H_4SO_2N(p-CH_3OC_6H_4)CH=CHCOCF_3$ ², mp 114-115°C. Presumably, acetyl group is not sufficient to cause immediate deprotonation from a possible intermediate (or transition state), $-\overset{\ddagger}{C}H-CH_2COCH_3$, and therefore, if it were formed, it would decompose or go back to the starting olefin⁸.

Mechanistic study of the present reaction is now in progress in our laboratory.

REFERENCES AND NOTES

1. M. Hojo, R. Masuda, and Y. Kamitori, *Tetrahedron Lett.*, 1009 (1976); M. Hojo, and R. Masuda, *J. Org. Chem.*, **40**, 963 (1975).
2. All these new compounds showed satisfactory elemental analyses (C, H, F or C, H, N, Cl) and spectral data (nmr, ir) consistent with the proposed structures.

3. Not determined yet as to geometrical isomerism.
4. It is reported in a patent that ethyl vinyl ether reacts with phosgene to give β -ethoxyacryloyl chloride (46 % yield) together with 1-chloroethyl ethyl ether (38 % yield) [R. E. Paul and S. Tchelitcheff, USP 2,768,174 (1956); Chem. Abstr., 51, 5818 (1957)].
5. For a review, see A. G. Cook, Ed., " Enamines: Synthesis, Structure and Reactions", Marcel Dekker, New York, 1969.
6. Although iminium ions are isolable in the case of acetylation of enamines⁵, no indication implying intermediacy of such a species was observed in the present reactions of vinyl sulfides¹, vinyl ethers and vinyl amides, at least in some runs followed carefully by nmr.
7. The mixed anhydride is a stronger acetylating reagent than acetic anhydride and not a trifluoroacetylating reagent. For a review, see L. F. Fieser and M. Fieser, " Reagents for Organic Synthesis ", John Wiley and Sons, Inc., New York, 1967, p. 1222.
8. The mixed anhydride is reported to react with simple olefins to give addition products, from which trifluoroacetic acid is eliminated by refluxing in methanol to yield acetylated olefins [A. L. Henne and J. M. Tedder, J. Chem. Soc., 3628 (1953)].

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