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ELECTROPHILIC SUBSTITUTIONS OF OLEFINIC HYDROGENS : ACYLATION OF 1,1-BISALKYLTHIO-1,3-ALKADIENES AND TRANS-N-ACETYL-N-ISOPROPYL-1-AMINO-1,3-BUTADIENE

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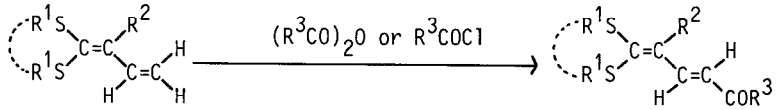
Summary : Reactions of the title compounds with trifluoroacetic anhydride and trichloroacetyl chloride occurred regioselectively to give corresponding 4-triholoacetylated compounds in excellent yields. In contrast, 1,1-bisethylthio-1,3-hexadiene gave preferentially 2-acylated compounds.

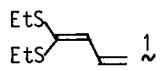
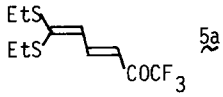
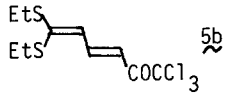
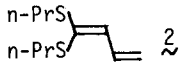
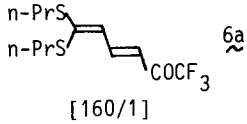
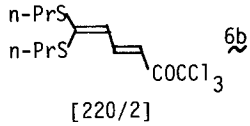
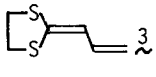
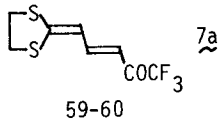
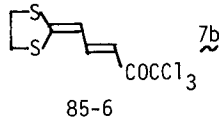
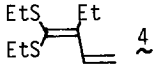
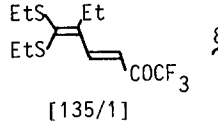
In our preceding papers it was reported that ketene dithioacetals[1,2], vinyl sulfides[1,2], vinyl ethers[3], N-vinyl amides[2,3], and N-vinylcarbazole[2] react with trihaloacetic anhydrides, oxalyl chloride, and ethoxalyl chloride quite easily at room temperature to afford corresponding β-acylated compounds in high yields. Moreover, the reactions of trithioorthoacetates[4], ethyl orthoacetate[5] and methyl ketone acetals[5] with these trihaloacetylating reagents also gave β-acylketene dithioacetals, β-acylketene acetals, and α-substituted β-acylvinyl ethers, respectively, in excellent yields. As an extension of these works to some butadiene systems we have examined these electrophilic substitutions of olefinic hydrogens with the title compounds. Expectedly, trihaloacetylation occurred easily under mild conditions in fair yields and we now wish to communicate these results.



1 - 4 (R^1= Et, n-Pr, $-CH_2-$; R^2= H, Et; R^3= CF_3, CCl_3) 5 - 8

In a typical experiment, to a stirred mixture of 1,1-bisethylthio-1,3-butadiene 1[6](2512.4 mg, 14.4 mmol) and pyridine (2285.3 mg, 28.9 mmol) in chloroform (90 ml) was added dropwise 6445.5 mg (30.7 mmol) of trifluoroacetic anhydride at room temperature and the solution was allowed to stand for 7 h. After usual work-up and distillation in vacuo there was obtained a 67% yield (2612.8 mg) of 4-trifluoroacetylated compound 5a: bp 140 °C/1 torr (oven temperature); N.M.R. (δ,$CDCl_3$): 8.08 (dd, 1H, J=11.0, 15.0 Hz), 6.34 (d, 1H, J=11.0 Hz), 6.23 (d, 1H, J=15.0 Hz), 2.91 (q, 4H, J=7.2 Hz), 1.33 (t, 3H, J=7.2 Hz), 1.28 (t, 3H, J=7.2 Hz); I.R. (film, cm^{-1}): $\nu_{C=O}$ 1685, $\nu_{C=C}$ 1560; Anal (%): Calcd. for $C_{10}H_{13}F_3S_2O$: C, 44.43; H, 4.85; F,

Table 1. Acylation of 1,1-Bisalkylthio-1,3-butadienes

Entry	Reactant	Acylating reagent	Reaction conditions[a] (°C)	(h)	Product mp (°C) or [bp(°C/torr)]	Yield(%)[b]
1	 1	$(CF_3CO)_2O$	rT	7	 5a	67
					[140/1]	
2	1	$(CCl_3CO)_2O$	rT	48	 5b	73
					[200/2]	
3	1	$(CCl_3CO)_2O$	50	17	5b	77
4	1	CCl_3COCl	50	17	5b	66
5	 2	$(CF_3CO)_2O$	rT	7	 6a	43
					[160/1]	
6	2	CCl_3COCl	50	17	 6b	76
					[220/2]	
7	 3	$(CF_3CO)_2O$	rT	2	 7a	100
					59-60	
8	3	CCl_3COCl	rT	24	 7b	54
					85-6	
9	 4	$(CF_3CO)_2O$	rT	18	 8	74
					[135/1]	

[a] Molar ratio, [substrate]/[acylating reagent]/[pyridine]: Entries 1-6, 1/2/2; Entries 7 and 8, 1/1.2/1.2; Entry 9, 1/3/2.

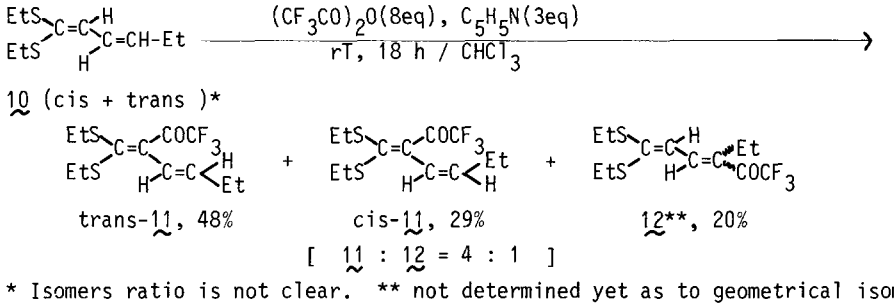
[b] Yields of isolated products.

21.08: Found: C, 44.14; H, 4.77; F, 21.53. The results of the trihaloacetylation are summarized and shown in Table 1. The 2-ethyl derivative 4 also reacted with three times molar amounts of trifluoroacetic anhydride at room temperature for 18 h to give 8 in 74% yield: bp 135 °C/1 torr (oven temperature); N.M.R. (δ,$CDCl_3$): 8.43 (d, 1H, J=15.5 Hz), 6.32 (d, 1H, J=15.5 Hz), 3.13-2.50 (m, 6H), 1.40-0.92 (m, 9H); I.R. (film, cm^{-1}): $\nu_{C=O}$ 1650, $\nu_{C=C}$ 1560; Anal (%): Calcd. for $C_{12}H_{17}F_3S_2O$: C, 48.30; H, 5.74; F, 19.10: Found: C, 48.55; H, 5.77; F, 19.13.

Interestingly, 1-3 were trihaloacetylated regioselectively at the 4-position without any acylation at the 2-position. Although it is not certain at present why this acylation can take place only at the terminal carbon, it may be due to steric hindrance. Compounds 1-4 gave exclusively trans acylated isomers, in contrast to the case of vinyl sulfides[1] where both cis and trans isomers were obtained invariably. Attempted reaction of 1 with acetyl chloride failed.

The trifluoroacetylations of compounds 1, 3, and 4 were followed spectroscopically by ^{1}H-N.M.R.[7] at room temperature in $CDCl_3$ as solvent. After 0.5 h 71% of 1 was acylated, while the reaction of 3 was completed within 10 minutes. Introduction of an Et group at the 2-position of 1 caused much decrease in rate and the reaction of 4 proceeded only in 40% even after 55 h. Comparison of the rate of the vinylog 1 with that of the parent compound $(EtS)_2C=CH_2$ 9[8] attracted our particular interest. Under the same condition, 9 was completely acylated within a few minutes. These differences in reactivity were magnified when an weaker acylating reagent was used. Thus trichloroacetylation with the use of trichloroacetyl chloride under the same condition as above proceeded as follows: 1, 50 h, 55%; 3, 4 h, 56%; 9, 10 min, 87%.

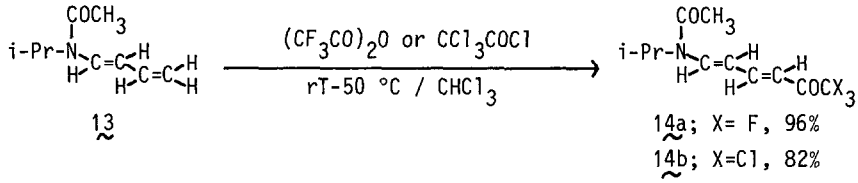
It was reported earlier[1] that trifluoroacetylation of vinyl sulfides is practically inhibited by introducing substituents at the β-position. In order to check for this effect in the present system 10 was allowed to react with twice molar amounts of trifluoroacetic anhydride at room temperature for 18 h to result in complete recovery of the starting material. Therefore the reagent was increased to eight times molar amounts, which gave cleanly trans-11, cis-11, and 12 in 48, 29, and 20% yields[9], respectively. It seems noteworthy that the reaction of 10 occurred preferentially at the internal position of the diene system, not the terminal as is the case of 1.



* Isomers ratio is not clear. ** not determined yet as to geometrical isomerism

Trifluoro- and trichloroacetylation of trans-N-acetyl-N-isopropyl-1-amino-1,3-butadiene

13[10] occurred regio- and stereoselectively, as was the case of 1-3, giving 14a, mp 92-3 °C, and 14b, mp 124-5 °C in 96 and 82% yields, respectively.



13

14a; X= F, 96%

14b; X=Cl, 82%

Further works are now in progress in our laboratory, especially from the mechanistic standpoint of view.

References and Notes

1. M. Hojo, R. Masuda, and Y. Kamitori, Tetrahedron Lett., 1009 (1976).
2. M. Hojo, R. Masuda, H. Sano, and M. Saegusa, Synthesis in press.
3. M. Hojo, R. Masuda, Y. Kokuryo, H. Shioda, and S. Matsuo, Chem. Lett., 499 (1976).
4. M. Hojo and R. Masuda, J. Org. Chem., 40, 963 (1975).
5. M. Hojo, R. Masuda, and E. Okada, submitted to Synthesis.
6. Compounds 1-3 and 10 were prepared according to the method of T. Oida [Thesis, Kyoto University, Japan (1983)], and 4 was prepared by a modified procedure based on the above method.
7. A solution of 1, 3, 4, or 9 (0.43 mmol) and pyridine-d_5 (0.43 mmol) in $CDCl_3$ (1.0 ml) was mixed with 0.43 mmol of the trihaloacetylating reagents in a N.M.R. tube at room temperature and its N.M.R. spectrum was recorded at appropriate time intervals. Conversions were determined by following disappearance of peaks for the two terminal olefinic hydrogens.
8. Prepared by the procedure of H. C. Volger and J. F. Arens, Recl. Trav. Chim. Pays-Bas, 76, 847 (1957).
9. Yields were determined by N.M.R. spectrum of the crude mixture. Inspection of the N.M.R. spectrum for this mixture showed that this reaction proceeded cleanly without formation of any detectable amounts of other materials. These three products could be separated by column chromatography on silica gel as follows: product, eluent, isolated yield (%); trans-11, n-hexane, 34; cis-11, subsequent n-hexane, 17; 12, n-hexane/benzene (7/3), 20.
10. Prepared according to the synthetic method of W. Oppolzer, L. Bieber, and E. Francotte, Tetrahedron Lett., 981 (1979).

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