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THE REACTIONS OF DIFLUORO AND DIBROMOKETENES WITH SILYLATED
KETENE ACETALS*

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SUMMARY

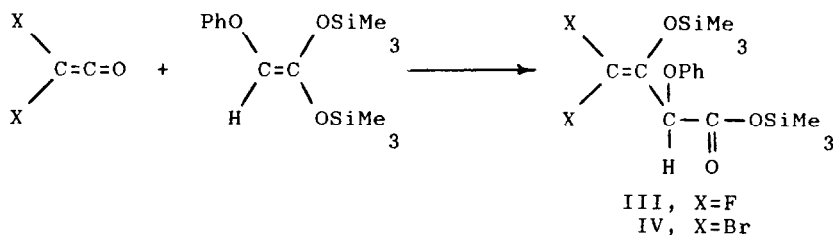
The in situ generation of difluoro- or dibromoketene from the corresponding acetyl chlorides and activated zinc in the presence of O-silylated ketene acetals at 45-50 °C temperature resulted in the formation of acyclic esters. All the results are consistent with a two step process involving a dipolar intermediate.

INTRODUCTION

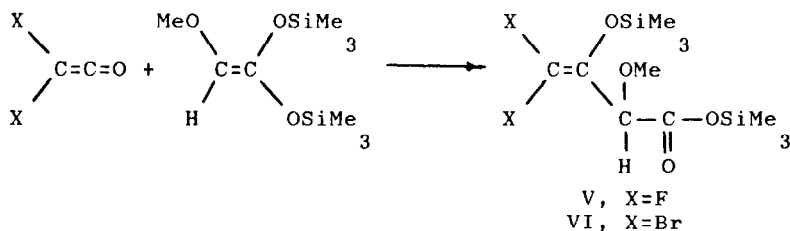
We have recently reported on the [2+2] cycloaddition reactions of halogenated ketenes with trimethylsiloxy cycloolefins [1]. The bicyclo products were isolated in good yields. We now wish to describe the reaction of difluoro and dibromoketenes with some readily available O-silylated ketene acetals to yield an acyclic unsaturated esters [2,3,4].

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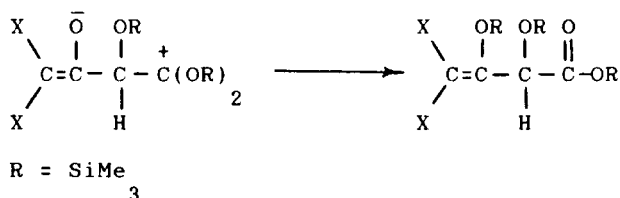
This paper is dedicated to Chemical Engineer Alireza Afzalipour the founder of Shaheed Bahonar University.



2-Methoxy-1,1-bis(trimethylsiloxy)ethene reacted with difluoroketene, generated by the activated zinc, dehalogenation of chlorodifluoro acetyl chloride, to yield an acyclic ester, trimethylsilyl-4,4-difluoro-3-trimethylsiloxy-2-methoxy-3-butenolate V. The ester was formed in 50% yield, was liquid and distilled under reduced pressure.



It would appear that dihaloketene reactions with electron-rich olefins occur through a two-step dipolar intermediate as originally proposed by Scarpati and co-workers [7]. The dipolar intermediate achieves stabilization by a 1,5 silyl migration from the oxygen of the ketene to yield the unsaturated ester.



Dibromoketene was obtained in situ by dehalogenation of tribromoacetyl chloride with zinc. It reacts readily with silylated ketene acetals to give exclusively acyclic

products. There was no evidence of any cycloaddition reaction. Apparently halogen atoms in the dihaloketenes do not markedly influence the reactivity in these reactions. Therefore these ketenes exhibit about the same reactivity.

EXPERIMENTAL

Trimethylsilyl-4,4-difluoro-2,3-bis(trimethylsiloxy)-3-buten-
oate I. From 25 mmol (3.7 g) portion of chlorodifluoro acetyl chloride and 25 mmol (7.3 g) of tris(trimethylsiloxy)ethene was isolated 5.8 g (60%) of I which distilled at 67-70 °C (0.4 torr); IR (neat) 1780 (C=O), 1640 cm⁻¹ (C=C); ¹H NMR δ 0.1 (s, 9 H), 0.15 (s, 9 H), 0.2 (s, 9 H), 4.7 (s, 1 H); ¹⁹F NMR δ 65.5 (m). Anal. Calcd for C₁₃H₂₈F₂O₂Si₄: C, 42.16; H, 7.52. Found: C, 42.45; H, 7.71.

Trimethylsilyl-4,4-dibromo-2,3-bis(trimethylsiloxy)-3-buten-
oate II. A 25 mmol (7.8 g) portion of tribromoacetyl chloride and 25 mmol (7.3 g) of tris(trimethylsiloxy)ethene were reacted to give 8.12 g (66%) of II b.p. 70-73 °C (0.1 torr): IR (neat) 1770 (C=O), 1640 cm⁻¹ (C=C); ¹H NMR δ 0.1 (s, 9 H), 0.16 (s, 9 H), 0.2 (s, 9 H), 5.24 (s, 1 H). Anal. Calcd for C₁₃H₂₈Br₂O₂Si₄: C, 31.70; H, 5.69. Found: C, 31.87; H, 5.75.

Trimethylsilyl-4,4-difluoro-3-trimethylsiloxy-2-phenoxy-3-
butenoate III. This adduct, III obtained from the reaction of 25 mmol (3.70 g) chlorodifluoroacetyl chloride and 25 mmol (7.35 g) of 2-phenoxy-1,1-bis(trimethylsiloxy)ethene, distilled at 99-104 °C (0.1 torr) to give 5.8 g (62%): IR (neat) 1780 (C=O), 1640 cm⁻¹ (C=C); ¹H NMR δ 0.20 (s, 9 H), 0.28 (s, 9 H), 5.13 (s, 1 H), 6.87 (m, 5 H), ¹⁹F NMR; δ 64.3 (m).

Anal. Calcd for $C_{16}H_{24}F_2O_2Si_2$: C, 51.34; H, 6.42. Found :
C, 50.98; H, 6.51.

Trimethylsilyl-4,4-dibromo-3-trimethylsiloxy-2-phenoxy-3-

butenoate IV. Reaction of a 25 mmol (7.8 g) tribromoacetyl chloride and 25 mmol (7.35 g) of 2-phenoxy-1,1-bis(trimethylsiloxy)ethene yielded IV which distilled at 128-130 °C (0.1 torr) to give 6.8 g (55%): IR (neat) 1770 (C=O) 1640 cm^{-1} (C=C); 1H NMR δ 0.1 (s, 9 H), 0.2 (s, 9 H), 5.48 (s, 1 H), 6.82 (m, 5 H).

Anal. Calcd for $C_{16}H_{24}Br_2O_2Si_2$: C, 38.70; H, 4.84. Found :
C, 39.16; H, 4.90.

Trimethylsilyl-4,4-difluoro-3-trimethylsiloxy-2-methoxy-3-

butenoate V. From 25 mmol (3.70 g) portion of chlorodifluoroacetyl chloride and 25 mmol (5.85 g) of 2-methoxy-1,1-bis(trimethylsiloxy)ethene was isolated 3.90 g (50%) of V which distilled at 70-74 °C (0.4 torr): IR (neat) 1780 (C=O), 1640 cm^{-1} (C=C); 1H NMR δ 0.05 (s, 9 H), 0.1 (s, 9 H), 3.19 (s, 3 H), 4.62 (s, 1 H); ^{19}F NMR δ 66.5 (m).

Anal. Calcd for $C_{11}H_{22}F_2O_2Si_2$: C, 42.30; H, 7.05. Found:
C, 41.96; H, 7.22.

Trimethylsilyl-4,4-dibromo-3-trimethylsiloxy-2-methoxy-3-

butenoate VI. This adduct, obtained from the reaction of 25 mmol (7.8 g) of tribromoacetyl chloride and 25 mmol (5.8 g) of 2-methoxy-1,1-bis(trimethylsiloxy)ethene, distilled at 75-78 °C (0.3 torr) to give 4.2 g (39%): IR (neat) 1770 (C=O), 1640 cm^{-1} (C=C); 1H NMR δ 0.05 (s, 9 H), 0.1 (s, 9 H), 3.2 (s, 3 H), 5.03 (s, 1 H).

Anal. Calcd. for $C_{11}H_{22}Br_2O_2Si_2$: C, 30.41; H, 5.07. Found:
C, 30.65; H, 4.84.

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