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CYCLOADDITION OF DIHALOKETENES WITH TRIMETHYLSILOXYCYCLOOLEFINS AND FLUORINATION OF THE PRODUCTS

M.H.HABIBI*

Department of Chemistry, Esfahan University, Esfahan, 81745 (Iran)

K.SAIDI

Department of Chemistry,Kerman University, Kerman, (Iran)

and L.C. SAMS

Department of Chemistry, Texas Woman's University, Denton, Texas, 76204 (U.S.A.)

SUMMARY

The generation of difluoro-, dichloro-, and dibromoketene by the activated zinc dehalogenation of the corresponding acetyl chlorides in the presence of trimethylsiloxycycloolefins were found to yield (2+2) cycloaddition products in good yield. Subsequently, the trimethylsiloxy groups of the products were replaced by fluorine with phenyltetrafluorophosphorane, a selective fluorinating agent.

INTRODUCTION

A number of reports have appeared in recent years on the cycloaddition of ketenes to olefins [1] . However, there are no reports involving the cycloaddition of dihaloketenes to siloxycycloolefins.

RESULTS AND DISCUSSION

This report details the [2+2] cycloaddition of dihaloketenes with activated olefins and fluorination of the products. Cycloaddition products

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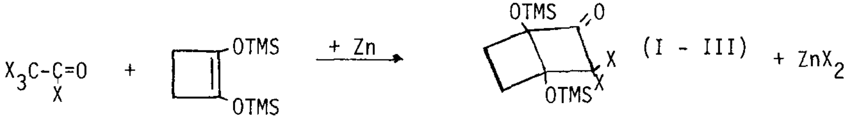
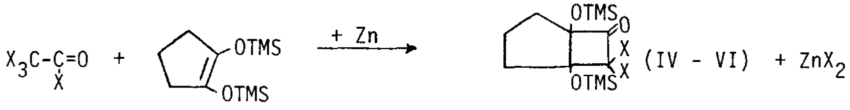
were isolated from the reaction of acetyl chlorides and 1,2-bis(trimethylsiloxy)cycloolefins in good yield. The products were then reacted with phenyltetrafluorophosphorane, which is a selective fluorinating agent to replace the trimethylsiloxy groups with fluorine.

The mixing of equimolar quantities of acetyl chlorides and 1,2-bis (trimethylsiloxy)cyclobutene under a nitrogen atmosphere produced from 34 to 65% yield of the 6,6-dihalo-1,4-bis(trimethylsiloxy)bicyclo[2.2.0] hexane-5-one(I-III).



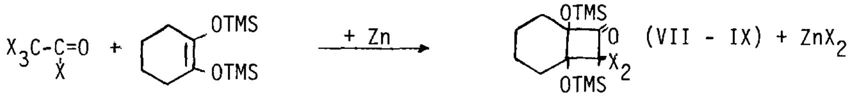
I, X = F ; II, X = Cl ; III, X = Br ; TMS = $SiMe_3$

The in situ cycloaddition of dihaloketenes with 1,2-bis(trimethylsiloxy)cyclopentene was allowed to proceed overnight and 7,7-dihalo-1,5-bis(trimethylsiloxy)bicyclo[3.2.0] heptane-6-one(IV-VI) were isolated in 47 to 75% yield.



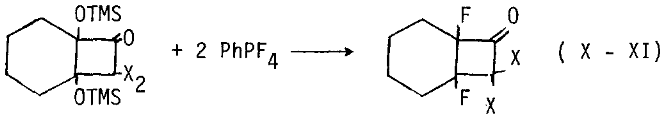
IV, X = F; V, X = Cl; VI, X = Br; TMS = $SiMe_3$

The mixing of equimolar quantities of acetyl chlorides and 1,2-bis-(trimethylsiloxy)cyclohexene under a nitrogen atmosphere after 12 hours afforded 8,8-dihalo-1,6-bis(trimethylsiloxy)bicyclo [4.2.0] octane-7-one (VII-IX).



VII, X = F; VIII, X = Cl; IX, X = Br; TMS = $SiMe_3$

Treatment of cycloaddition products with $PhPF_4$ resulted in replacement $OSiMe_3$ groups with fluorine without attack on the carbonyl bond.



X, X = F; XI, X = Cl

The products were characterized by ^{19}F-NMR,^{1}H-NMR,and IR spectral,and elemental analysis.

EXPERIMENTAL

Trichloroacetyl chloride and chlorodifluoroacetyl chloride were purchased from Aldrich Chemical Company and Organic Chemical Company,respectively . Tribromoacetic acid was bought from Fluka Chemical Company. Fluorine and proton nuclear magnetic resonance spectra were recorded on Varian EM-390 spectrometer using $CFCl_3$ as internal reference and tetramethylsilane as external standard. The mass spectrum was determined with a Consolidated Electrodynamics Corporation Model 21-104 mass spectrometer. IR spectra were recorded with a Perkin-Elmer Model 225 infrared spectrophotometer using a 0.1 mm liquid cell fitted with polyethylene windows.Analytical samples were obtained, where possible, by vapor phase chromatography on a Varian 90P-3 gas chromatograph fitted with a 3/8 inch 20 foot column packed with 30% SE-30 on Chromosorb P. Ether, hexane, and heptane were distilled from sodium under a nitrogen atmosphere.The zinc was activated by a standard procedure [2] and was always stored and used under a nitrogen atmosphere. Tribromoacetyl chloride was prepared from tribromoacetic acid and either thionyl chloride or oxalyl chloride. Siloxycycloolefins were prepared by the literature procedure [3] and were freshly distilled prior to each reaction.

Typical Procedure for Cycloaddition of Dihaloketenes with Siloxycyclo-olefins: 6,6-Difluoro-1,4-bis(trimethylsiloxy)bicyclo[2.2.0] hexane-5-one(I). A 500 ml, 1-neck round-bottomed flask fitted with a condenser, magnetic stirrer and dropping funnel equipped with a pressure-equalizing side arm was charged with 25 mmol (5.75g) of 1,2-bis(trimethylsiloxy)cyclobutene in 200 mL ethyl acetate and 7.0g activated zinc under a nitrogen atmosphere. A solution of 25 mmol (3.72g) of chlorodifluoroacetyl chloride in 200 mL of dry ethyl acetate was added very slowly (10-12 hours) to the stirred mixture at 40°C. At the completion of the reaction period, the excess zinc was removed by the filtration. The solution was concentrated to about 10 ml by means of a rotary evaporator, the residue was dissolved in 50 mL of dry hexane, decanted, vacuum distilled and further characterized. After distillation of 41-45°C at 0.3 Torr, yield 2.62 g (34%). IR: 2995, 1800 (C=O), 1165 cm^{-1}; ^{1}H-NMR: δ=2.0

(m, 4H), 0.45 (m, 9H), 0.2 (m, 9H); ^{19}F-NMR: δ = 65 (d, 1F), 65.8 (d, 1F); Mass spectrum = m/e 308 (5.4), 293 (21), 73 (100).

Anal. Calcd. for $C_{12}H_{22}F_2O_3Si_2$ = C, 46.75; H, 7.14. Found = C, 46.36; H, 6.73.

6,6-Dichloro-1,4-bis(trimethylsiloxy)bicyclo[2.2.0]hexane-5-one (II). This product was prepared by cycloaddition of 25 mmol (4.65 g) of trichloroacetyl chloride, 7.0 g of activated zinc and 25 mmol (5.75 g) of 1,2-bis-(trimethylsiloxy)cyclobutene in 450 mL of dry ether. After distillation at 60-64°C (0.4 Torr), yield 4.69 g (55%). IR: 2980, 1790 (C=O), 1150 cm^{-1}; ^{1}H-NMR: δ= 1.9 (m, 4H), 0.15 (m, 9H), 0.03 (m, 9H).

Anal. Calcd. for $C_{12}H_{22}Cl_2O_3Si_2$: C, 42.23; H, 6.45. Found: C, 42.56; H, 6.71.

6,6-Dibromo-1,4-bis(trimethylsiloxy)bicyclo[2.2.0]hexane-5-one (III). By the general procedure, 25 mmol (7.88 g) of tribromoacetyl chloride (m.p. = 45°C), 7.0 g of activated zinc and 25 mmol (5.75 g) of 1,2-bis(trimethylsiloxy)cyclobutene,after distillation at 66-69°C (0.25 Torr), yield 45%. IR: 2970, 1780 (C=O), 1165 cm^{-1}; ^{1}H-NMR: δ = 1.68 (m, 4H), 0.15 (m, 9H), 0.00 (m, 9H).

Anal. Calcd. for $C_{12}H_{22}Br_2O_3Si_2$: C, 33.49; H,5.15. Found: C, 33.86; H, 5.37.

7,7-Difluoro-1,5-bis(trimethylsiloxy)bicyclo[3.2.0]heptane-6-one(IV). A 0.025 mol portion of chlorodifluoroacetyl chloride, 7.0 g of activated zinc and 0.025 mol (6.10 g) of 1,2-bis(trimethylsiloxy)cyclopent-1-ene in 400 mL of dry ether after distillation at 48-52° C at 0.05 Torr, yielded 3.94 g (47%). IR: 3000, 1800 (C=O), broad band at 1160 and 985 cm^{-1}; ^{1}H-NMR: δ = 1.9 (t, 4H), 1.4 (m, 2H), 0.2 (s, 18H); ^{19}F-NMR: δ= 163.2 (d) with respect to $CFCl_3$ as internal standard. Mass spectrum, m/e 322 (3.2), 307 (11.4), 233 (7.8), 79 (95), 73 (100).

Anal. Calcd. for $C_{13}H_{24}O_3F_2Si_2$: C, 48.44; H, 7.45. Found: C, 48.60; H, 7.65.

7,7-Dichloro-1,5-bis(trimethylsiloxy)bicyclo[3.2.0]heptane-6-one (V). This compound distilled at 72-76°C (0.3 Torr), (75%). IR: 2960, 1750 (C=O), 1260, 850 cm^{-1}; ^{1}H-NMR: δ= 2.0 (m, 2H), 0.2 (m, 9H), 0.03 (m, 9H).

Anal. calcd. for $C_{13}H_{24}Cl_2O_3Si_2$: C, 43.88; H, 6.70. Found: C, 43.50; H, 6.82.

7,7-Dibromo-1,5-bis(trimethylsiloxy)bicyclo[3.2.0]heptane-6-one (VI). Distillation occurred at 82-85°C (0.25 Torr), (74%). IR: 2975, 1765, (C=O), 1270 780 cm^{-1}; ^{1}H-NMR: δ = 1.80 (m, 4H), 1.63 (m, 2H), 0.2 (m, 9H), 0.03 (m, 9H).

Anal. calcd. for $C_{13}H_{24}Br_2O_3Si_2$: C, 35.13; H, 5.32. Found: C, 35.44; H, 5.69.

8,8-Difluoro-1,6-bis(trimethylsiloxy)bicyclo[4.2.0] octane-7-one (VII).

A 0.025 mol (3.72 g) portion of chlorodifluoroacetyl chloride, 7.0 g of activated zinc and 0.025 mol (6.45 g) of 1,2-bis(trimethylsiloxy)cyclohex-1-ene in 400 mL of dry ether after distillation at 52-55^{o}C at 0.04 Torr, yielded 4.62 g (55%). IR: 2980, 1795 (C=O) and 1150 cm^{-1}. ^{1}H-NMR: δ = 1.5 (m, 8H), 0.2 (s, 18H). ^{19}F-NMR: δ = 164 (d). Mass spectrum, m/e 336 (2.7), 263 (9.6), 73 (100).

Anal. Calcd. for $C_{14}H_{26}O_3F_2Si_2$: C, 50.0; H, 7.74. Found: C, 50.23; H, 7.92.

8,8-Dichloro-1,6-bis(trimethylsiloxy)bicyclo[4.2.0]octane-7-one (VIII).

This compound distilled at 105-108^{o}C (0.35 Torr), (65%). IR: 2980, 1795 (C=O), and 1150 cm^{-1}. ^{1}H-NMR: δ=2.00 (m, 4H), 1.63 (m, 4H), 0.45 (m, 9H), 0.2 (m, 9H).

Anal. calcd. for $C_{14}H_{26}Cl_2O_3Si_2$: C, 45.51; H, 7.09. Found: C, 45.27 ; H, 7.13.

8,8-Dibromo-1,6-bis(trimethylsiloxy)bicyclo[4.2.0]octane-7-one (IX).

Distillation occurred at 95^{o}C (0.2 Torr), (82%). IR: 2970, 1750 (C=O), 1270, 785 cm^{-1}. ^{1}H-NMR: δ= 1.95 (m, 4H), 1.50 (m, 4H), 0.3 (m, 9H), 0.06 (m, 9H).

Anal. Calcd. for $C_{14}H_{26}Br_2O_3Si_2$: C, 36.68; H, 5.68. Found: C, 37.12 ; H, 5.84.

General Procedure for Selective Fluorination of Cycloaddition Products:

To a stirred solution of 20 mmol of cycloaddition products in a 25 mL two-necked flask equipped with a dropping funnel with side arm, and a reflux condenser connected to a nitrogen flow, was added 40 mmol of phenyltetrafluorophosphorane ($PhPF_4$) in a period of one hour. The products were detected by gas chromatography and identified by ^{1}H-NMR, ^{19}F-NMR, IR, and elemental analysis. 1,6,8,8-Tetrafluorobicyclo[4.2.0]octane-7-one (X).

This compound showed IR: 1795 cm^{-1} (C=O) ; ^{19}F-NMR: δ = 162.5 (d, 2F), 158 (m, 2F) ; ^{1}H-NMR: δ= 2.35 (m, 4H), 2.81 (m, 4H).

Anal. Calcd. for $C_8H_8F_4O$: C, 48.98; H, 4.08. Found: C, 48.51; H, 4.26.

8,8-Dichloro-1,6-difluorobicyclo[4.2.0]octane-7-one (XI).

This compound showed IR: 1790 cm^{-1} (C=O); ^{19}F-NMR: δ = 151 (m, 2F); ^{1}H-NMR: δ = 1.95 (m, 4H); 2.58 (m, 4H).

Anal. Calcd. for $C_8H_8Cl_2F_2O$: C, 41.92; H, 3.49. Found: C, 42.21; H, 3.61.

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