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Cycloaddition Reactions of Dichloroketene to Allyl Ethers

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Allyl ethers reacted with dichloroketene by [2+2] Cycloaddition to produce 2,2-dichlorocyclobutanones structure of products were determined by IR, NMR, GC MS techniques.

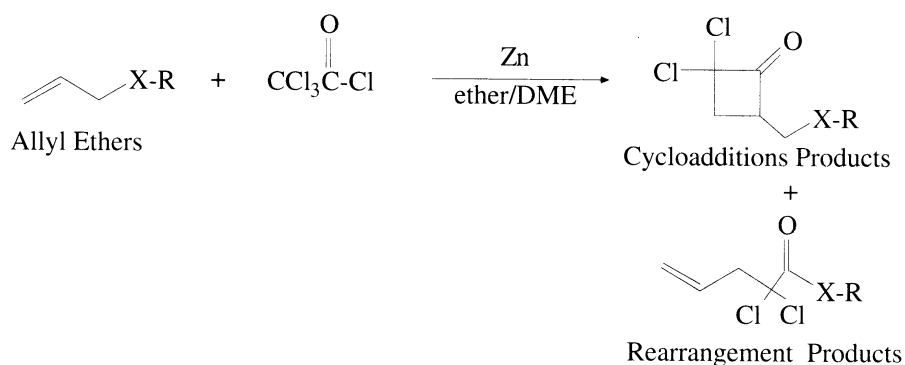
Introduction

Cyclobutanone derivatives were synthesized by [2+2] cycloaddition of ketene and olefines. Stereospecific [2+2] cycloaddition products were synthesized by the reactions of ketene with dienes¹. Bicyclo derivatives were synthesized by the cycloadditions of ketene with cyclic dienes. Bicyclo compounds were used as starting materials in organic synthesis.

A representative preparation is illustrated with dichloroketene and cyclopentadiene to yield the bicyclo[3.2.0] hept-2en-6-one followed by reductive removal of the chlorine atoms. This bicyclic compound has been found to be a versatile intermediate in prostaglandin synthesis. There are numerous other examples involving the use of bicyclo[3.2.0] heptan-6-ones in synthetic schemes leading to compounds of chemical and biological interest².

Dichloroketene or halogenated ketenes are generally more reactive in cycloaddition reactions than alkyl- or arylketenes. The cycloaddition products obtained from halogenated ketenes are useful synthetic intermediates because the halogen atom is easily replaced by hydrogen and, also since the halogen is a good leaving group, substitution and ring contraction reactions of the ketene cycloadducts become important. Another significant consideration is that the starting materials for the preparation of halogenated ketenes are inexpensive and they are readily available².

Cycloadditions of dichloroketene with allylic ethers, sulfides and selenides were investigated by a number of research groups. It has been reported that the dichloroketene reacts with allyl ethers and allyl sulfides to provide not only the expected [2+2] cycloaddition product, but also a (3,3) sigmatropic (Claisen) rearrangement product via 1,3-dipolar intermediate³. Both rearrangement and cycloaddition products were obtained when ether was used as solvent. Whereas only cycloaddition product was obtained when DME-ether mixture was used as solvent.

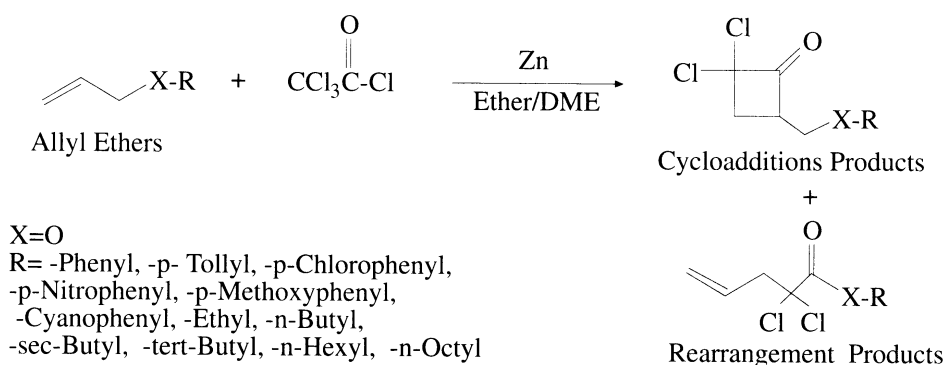


Dry ether was also used as solvent and observed that the rearrangement yield is more than the cycloaddition yield and some compounds did not give cycloaddition⁴. In this study cycloaddition of dichloroketene with allyl aryl ethers having different substituents on aromatic rings and with allyl alkyl ethers having different carbon contents were investigated.

Experimental

The ¹H-NMR spectra were recorded on a Bruker AC-200(200 MHz), Varian gemini (200 MHz) and Varian EM-360 (60 MHz) NMR spectrometers. *CDCl*₃ and DMSO-*d*₆ were used as solvents with tetramethylsilane as the internal standard. IR spectra were obtained on a Hitachi 270-30 spectrometer. GCMS spectra were recorded on 5890 Series 2 Gas Chromatography 5971 Series Mass Selective Detector Combine system. Ether and dimethoxyethane were dried by sodium-potassium alloy and purified by distillation prior to use. Zinc was activated by the method of Krepski⁵. Aryl allyl ethers were prepared by the reactions of *p*-X-phenols with allyl bromide. Allyl alkyl ethers were prepared by reactions of alkoxide of corresponding alcohols with allyl bromide^{6,7,8,9}.

General Procedure for the Cycloaddition of Dichloroketene with Allyl Ethers



A solution of the allyl ether or sulfide (0,02 mole) in anhydrous ether (40 cc) and 1,2-dimethoxyethane (40 cc) containing activated zinc 4,0 g (0,06 mole) and trichloroacetyl chloride 6,0 ml (0,0054 mole) were refluxed under helium atmosphere for 48 h. The reaction mixture was filtered and the excess Zn rinsed with anhydrous ether. The ether was removed in vacuo and the residue dissolved in hexane. Insoluble materials were removed by filtration and the filtrate was washed with saturated *NaHCO*₃ solution and with brine. After drying with anhydrous *MgSO*₄, the solvent was removed in vacuo and crude product as purified by chromatography on silica gel (Table 1).

2,2-Dichloro-4-(phenoxymethyl) cyclobutanone (1b): Obtained via thin-layer chromatography using 5% ethylacetate-hexane solvent mixture, 3,8 g (82 %). bp=145-147° C (5mm Hg) Lit bp=103-110° C (0,1mm Hg)

2,2-Dichloro-4-(p-tolyloxymethyl) cyclobutanone (2b): Pure compound (2b) (85%) was separated from (2c) via thin-layer chromatography using 5% ethylacetate-hexane. bp=148° C (5mm Hg)

IR (KBr): 2850-3050, 1810, 1450-1600, 1240 cm^{-1}

$^1\text{H-NMR}$ (60 MHz) (CDCl_3) δ (ppm): 6,8-7,3(m, 2H; m,2H,AA'BB'), 4,3(d,2H),3,4(m,3H), 2,4(s,3H).

Mass Spectra m/e: 258 (16), 216(9), 181 (14), 109 (100), 91 (25), 77(27).

Tolyl ester of 2,2-dichloro-4-pentenoic acid (2c): bp= 150° C (5mm Hg) Yield: 11%

IR (KBr): 2850-3050, 1765, 1450-1600, 1240 cm^{-1}

$^1\text{H-NMR}$ (60 MHz) (CDCl_3) δ (ppm): 6,8-7,2(m, 2H; m2H, AA'BB'), 5,4(d, 2H), 5,3(m,2H),4,4(d,2H),2,1(s,3H).

Mass Spectra m/e: 258(40), 159 (68), 147 (79), 108 (100), 91 (58), 77 (68).

2,2-Dichloro-4-(p-chlorophenoxymethyl) cyclobutanone (3b): Compounds (3b) and (3c) were separated via thin-layer chromatography using 5% ethylacetate-hexane solvent mixture.

bp=150° C (5mm Hg) Yield: 55%

IR (KBr): 2900-3100, 1810, 1450-1650, 1240 cm^{-1}

$^1\text{H-NMR}$ (60 MHz) (CDCl_3) δ (ppm): 6,8-7,2 (m, 2H; m2H, AA'BB'), 4,2 (d.d,2H), 3,0-3,3 (m,3H).

Mass Spectra m/e: 278 (12), 149 (22), 109 (100), 99 (18), 75 (22).

p-Chlorophenyl ester of 2,2-dichloro-4-pentenoic acid (3c): bp=160° C (5mm Hg)

Yield: 10%

IR (KBr): 2900-3100, 1765, 1450-1600, 1240 cm^{-1}

$^1\text{H-NMR}$ (60 MHz) (CDCl_3) δ (ppm): 6,8-7.5 (m, 2H; m2H, AA'BB') 5,4(d,2H), 5,2 (m,1H), 4,5 (d,2H)

Mass Spectra m/e: 278 (11), 128 (33), 111 (21), 75 (100), 39 (11).

2,2-Dichloro-4-[(p-methoxy)phenoxy methyl] cyclobutanone (6b): Compounds(6b) was purified via thin-layer chromatography using 25% ethylacetate-hexane mixed solvent.

mp=190° C Yield: 89%

IR (KBr): 2800-3050, 1810, 1400-1600, 1230 cm^{-1}

$^1\text{H-NMR}$ (60 MHz) (CDCl_3) δ (ppm): 6,8-7.0(s, 4H), 4,5(d,2H), 3.8(s,3H), 3,2-3,5(m,3H).

Mass Spectra m/e: 274 (17), 123 (100), 109 (12), 95 (197).

2,2-Dichloro-4-(n-butoxymethyl) cyclobutanone (7b): Compounds (7b) was purified via column chromatography using 5% ethylacetate-hexane mixed solvent.

bp=120° C (10 mm Hg) Yield: 85%

IR (KBr): 2800-2950, 1810, 1100-1200 cm^{-1}

$^1\text{H-NMR}$ (200 MHz) ($\text{DMSO} - d_6$) δ (ppm): 0,9(t,3), 1,2-1,6(m, 4H), 3,1 (d.d, 1H), 3,2 (d.d, 1H), 3.4-3.5 (m, 4H), 3.65 (d.d, 1H), 3.80 (d. d, 1H).

2,2-Dichloro-4-(sec-butoxymethyl) cyclobutanone (8b): Compound (8b) was purified via column chromatography using 5% ethylacetate- hexane mixed solvent.

bp: 90° C (0,02 mm Hg) Yield: 60%

IR (KBr): 2800-2950, 1812, 1100 cm^{-1}

$^1\text{H-NMR}$ (200MHz)(CDCl_3) δ (ppm): 0,9(t,3H), 1,0(d,3H), 1,3-1, 5 (m, 2H), 3,0 (m,1H), 3,1-3,2 (d, 2H), 3,4(m,6H), 3,6 (d,7H).

Mass Spectra (m/e): 168 (32), 133(59), 109(86), 57(95), 41(100), 29(90).

2,2-Dichloro-4-(ter-butoxymethyl) cyclobutanone (9b): Compound (9b) was purified via column chromatography using 5% ethylacetate- hexane mixed solvent.

bp=110 °C (10 mm Hg) yield: 70%

IR (KBr): 2800-2950, 1812, 1080 cm^{-1}

$^1\text{H-NMR}$ (200 MHz) (CDCl_3) δ (ppm): 1,4(s, 9H), 3,0-3,3 (m, 3H), 3,6-3,9(d.d, 2H).

Mass Spectra m/e: 209 (4), 109 (25), 57 (100), 41 (36).

2,2-Dichloro-4-(n-hexyloxymethyl) cyclobutanone (10 b): Compound (10b) was purified thinlayer chromatography using 20% ethylacetate-hexane mixed solvent.

bp=130 °C (8 mm Hg) yield: 86%

IR (KBr): 2850-3000, 1812, 1100 cm^{-1}

$^1\text{H-NMR}$ (60 MHz) (CDCl_3) δ (ppm): 3,8(d.d,1H), 3.65 (d.d, 1H), 3,4-3,5 (m, 3H),3,0-3,2 (5m, 2H), 1,6 (m, 2H), 1,3 (m, 6H), 0,9 (t, 3H).

Mass Spectra m/e: 253 (1), 168 (44), 133 (100), 122 (48), 109 (63) 43 (82).

2-2-Dichloro-4-(n-octyloxymethyl) cyclobutanone (11b): Compound (11b) was purified via thin-layer chromatography using 15% ethylacetate-hexane mixed solvent.

bp=135 °C (5mm Hg) Yield: 80 %

IR (KBr): 2800-3000, 1810, 1100 cm^{-1}

$^1\text{H-NMR}$ (200 MHz) (CDCl_3) δ (ppm): 3,8 (d.d, 1H), 3.65 (d.d, 1H), 3,4-3,5 (m, 3H), 3,0-3,2 (m, 2H), 1,6 (m, 2H), 1,2-1,4(m, 10H), 0,9 (t, 3H).

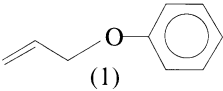
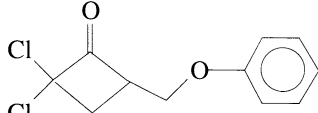
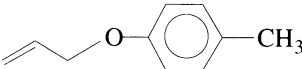
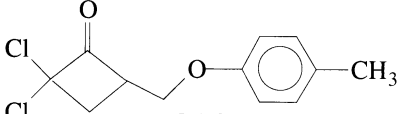
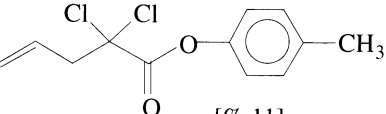
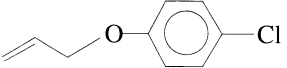
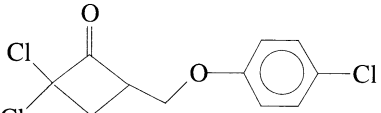
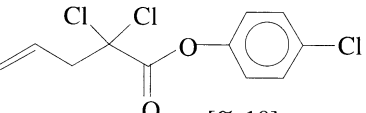
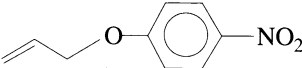
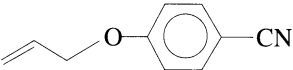
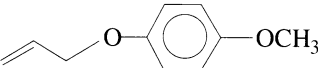
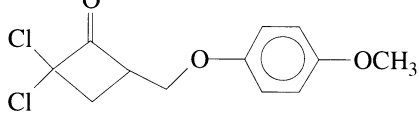
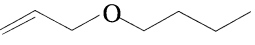
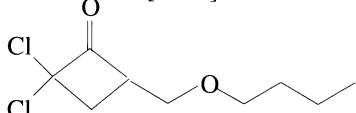
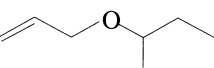
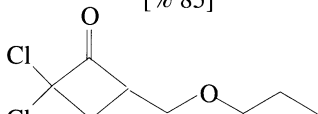
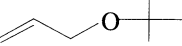
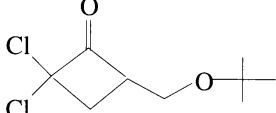
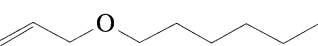
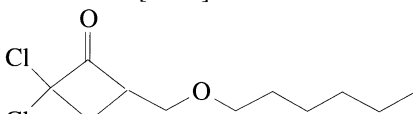
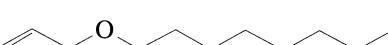
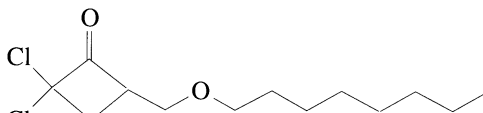
Result and Discussion

In this study at first allyl aryl ethers and allyl alkyl ethers were synthesized and reacted with dichloroketene. The syntheses of most of the ethers were reported in literature. Some new ethers were synthesized according to the literature procedures.

For the synthesis of n-, sec-, tert-butyl ethers a different solvent, i.e. dioxane, was used and increased yields as well as easily purified products were obtained. In Initial experiments dichloroketene was generated either by dehydrohalogenation of dichloroacetylchloride or by zinc dehalogenation of trichloroacetyl chloride. In the case of dehydrohalogenation, the low yields were attributed to the polymerization of dichloroketene by triethylammonium chloride¹⁰ which was produced during ketene formation. This approach was abandoned after methods to circumvent this problem by slow addition of reagents failed to give useful yields of adducts. In the case of the dehalogenation, low yields were attributed to ZnCl_2 induced side reactions. The proposed mechanism for the formation of the rearrangement products is a [3,3]-sigmatrope rearrangement of the initially formed dipolar intermediate.

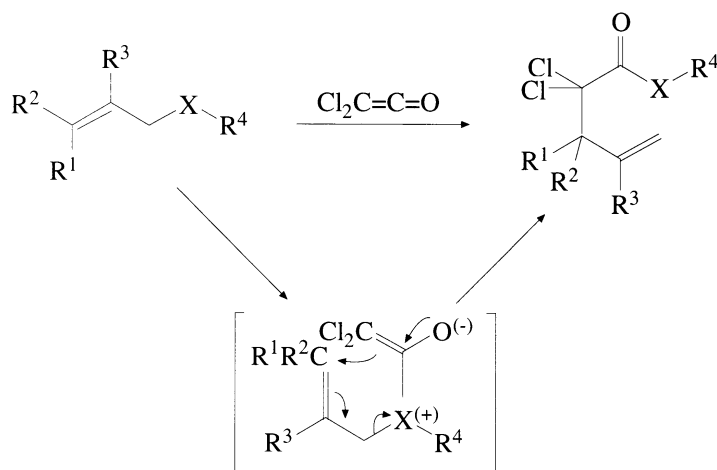
The cycloaddition reaction was carried out in dry ether and dry ether-DME solvent mixture and performed under helium atmosphere. When ether was used as solvent, only sigmatropic rearrangement was obtained. Also when the solvent was a mixture of DME-ether both cycloaddition and rearrangement were observed. When the amount of DME was increased in the DME-ether mixture, the cycloaddition yield increased. The ratio of the products did not change with DME-ether ratio. For each cycloaddition dichlorocyclobutanones were found to be the major products. Yields of the [2+2] cycloadditions were, for the most part, in the range of 55-89% although some of the products were unstable and tended to decompose during distillation or chromatography. (Table 1).

Table 1. Reaction of Dichloroketene with Allyl Ethers

Allyl ether (a)	Cycloaddition products (b) [Yields]	Rearrangement products (c) [Yields]
 (1)	 [% 82]	—
 (2)	 [% 85]	 [% 11]
 (3)	 [% 55]	 [% 10]
 (4)	—	—
 (5)	—	—
 (6)	 [% 89]	—
 (7)	 [% 85]	—
 (8)	 [% 60]	—
 (9)	 [% 70]	—
 (10)	 [% 86]	—
 (11)	 [% 80]	—

The products were isolated by thin-layer and column chromatography and boiling points were identified by the distillation of purified products. The molecular structures were identified by IR, NMR, GCMS spectroscopic techniques.

Allyl aryl ethers having $-Cl$, $-CH_3$, $-OCH_3$ on aromatic ring, gave cycloaddition products in high yields. Allyl aryl ethers having $p-Cl$ and $p-CH_3$ substituents gave 10% rearrangement products besides cycloaddition and the products were isolated. Phenyl and $p-OCH_3$ phenyl ethers gave only cycloaddition products. The reactions of $-NO_2$, and $-CN$ substituted aromatic ring with allyl aryl ether did not yield cycloaddition or rearrangement product. Rearrangement reaction proceeds by passing from an intermediate state that forms by nucleophilic attack of allylic oxygen on sp hybridized carbon atom of ketene³.



The $-NO_2$, and $-CN$ groups on the aromatic ring prevent the rearrangement reaction by withdrawing electrons on the oxygen atom mesomerically and so decreasing the nucleophilic character of oxygen atom attacks the electrons of the double bond by inductive effect thus the cycloaddition reaction doesn't proceed. A high yield of adducts of allyl alkyl ethers with dichloroketene and a small amount of rearrangement product were obtained. This product was determined by IR and GC MS spectra, but could not be isolated.

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