

CYCLOADDITIONS OF DICHLOROKETENE

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CYCLOADDITIONS OF DICHLOROKETENE

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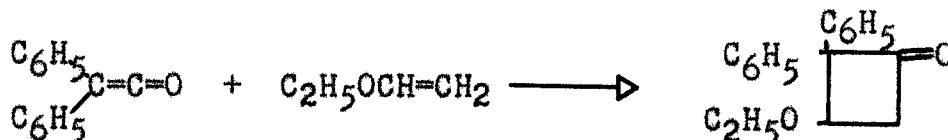
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CHAPTER I

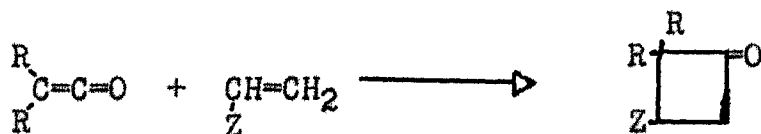
INTRODUCTION

In 1907 Staudinger reported the cycloaddition of diphenylketene and ethyl vinyl ether to form a substituted cyclobutanone (8).



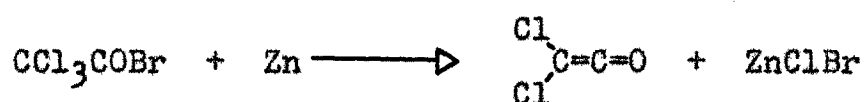
Staudinger later reported the cycloaddition of diphenylketene with styrene, cyclopentadiene, and cyclohexene to form the appropriately substituted cyclobutanones (9).

Since Staudinger's original investigations, an extensive amount of work has been reported on the cycloaddition reaction of ketenes. This reaction is now recognized as a characteristic reaction of ketenes. The ketenes most commonly employed are diphenylketene and dimethylketene with activated or nucleophilic olefins. Cycloadditions of diphenylketene and dialkylketenes with enamines, vinyl ethers, α, β -unsaturated ethers, and various olefins and dienes have been recently reported (3, 4, 5, 6, 7). This 1,2-cycloaddition may be generally represented as follows:

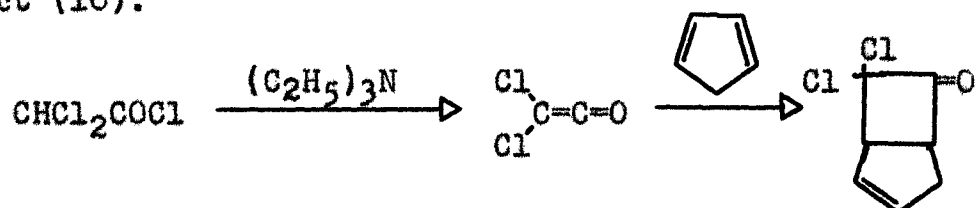


The facility of these reactions parallels the nucleophilicity of the olefins. For example, the reaction proceeds readily with olefins such as ethyl vinyl ether and dihydropyran, but proceeds with difficulty, if at all, with unactivated olefins such as cyclohexene. Cycloadditions involving unactivated olefins can be made to proceed under forcing conditions, but then only in low yield. There have been no reports of cycloadditions involving electrophilic or deactivated olefins, such as acrylonitrile.

Brady, Liddell, and Vaughn have quite recently reported the preparation of dichloroketene by the dehalogenation of trichloroacetyl bromide (1).

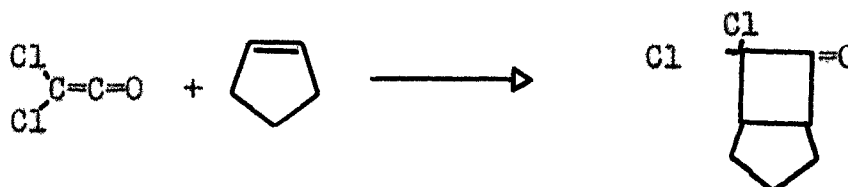


Stevens and co-workers have also recently reported the preparation of dichloroketene by dehydrohalogenation of dichloroacetyl chloride with triethylamine in the presence of cyclopentadiene and isolated the corresponding cycloadduct (10).



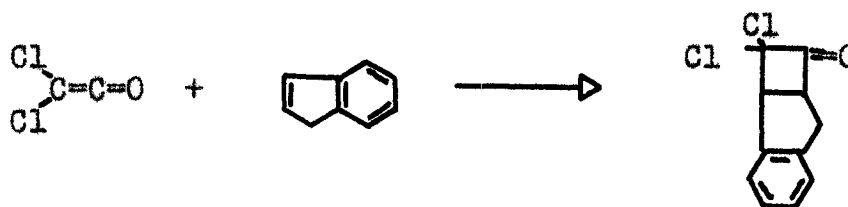
This adduct is a precursor to tropolone.

A recent communication by Ghosez and co-workers also describes the formation of the dichloroketene-cyclopentadiene adduct as well as the cycloaddition of dichloroketene and cyclopentene (2).



It was suggested that dichloroketene might be unique in that this ketene underwent cycloaddition with cyclopentene very readily and in good yield.

Turner and Seden have also quite recently reported the cycloaddition of dichloroketene and indene to produce a cycloadduct which is a precursor to 4,5-benzotropolone (11).



An investigation of the cycloaddition behavior of dichloroketene with various types of olefins seemed in order to determine if dichloroketene behaved similarly to dialkylketenes. It was anticipated that a study of this type would indicate the reactivity of dichloroketene to various types of olefinic compounds and thus establish if the ease of cycloaddition with dichloroketene parallels the nucleophilicity of the olefin as it does in dialkylketenes.

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CHAPTER II

EXPERIMENTAL

The infrared spectra were obtained by a Perkin-Elmer Model 237 Grating Infrared Spectrophotometer. Liquid samples were run as smears on sodium chloride discs. The proton magnetic resonance spectra were obtained by a Varian A-60 Nuclear Magnetic Resonance Spectrometer. The samples were run as 20 per cent solutions in chloroform with tetramethylsilane as a reference. Analyses were made by C. F. Geiger, Ontario, California, and Ed Hoff, Chemistry Department, North Texas State University, Denton, Texas.

Trichloroacetyl Bromide

The trichloroacetyl bromide was prepared from commercially available trichloroacetic acid and phosphorus tribromide. A 250 g. (1.53 moles) portion of trichloroacetic acid was placed in a 500 ml., one-necked flask equipped with a reflux condenser. A 181 ml. (515.7 g.; 1.91 moles) portion of phosphorus tribromide was added dropwise down the condenser to the trichloroacetic acid. When the addition was complete, the reaction solution was heated at reflux for three hours. The crude trichloroacetyl bromide was distilled on a 30-plate Oldershaw column. There was obtained 270 g.

(141-143°) of trichloroacetyl bromide, which corresponds to an 81 per cent yield.

Activation of Zinc

A 200 g. portion of zinc dust was added to 200 ml. of water in a 500 ml., three-necked flask equipped with a stirrer, and stirred vigorously. To this mixture was added 7.26 g. of hydrated copper sulfate dissolved in 50 ml. of water. This mixture was stirred for two hours. The activated zinc was then removed by filtration, washed several times with acetone, and dried in a vacuum oven at 100°C for several hours.

8,8-Dichlorobicyclo [4.2.0] octan-7-one

A mixture of 200 ml. of dry ether, 41.0 g. (0.63 mole) of zinc dust activated with copper, and 64.0 ml. (51.7 g.; 0.63 mole) of cyclohexene were placed in a reaction flask, and a solution of 28.0 g. (0.124 mole) of freshly distilled trichloroacetyl bromide in 50 ml. of dry ether was added dropwise with stirring to the mixture. At the conclusion of the exothermic reaction, the ether solution was separated from the unreacted zinc, and the ether solution extracted with 200 ml. of dry hexane, resulting in the precipitation of the zinc halide. The solution was decanted from the residue and the solvents were evaporated on a steam bath. The residue was distilled at reduced pressure to yield 10.5 g. of

8,8-dichlorobicyclo [4.2.0] octan-7-one at 93-94° (2.5 mm).

This corresponds to a 52 per cent yield.

Infrared absorption (smear): 1806 cm^{-1} (s).

Proton magnetic resonance: pair of multiplets centered at 4.1 p.p.m. and 2.9 p.p.m.; multiplet centered at 1.8 p.p.m.; peak areas in ratio of 1:1:8.

Analysis: Calcd. for $\text{C}_8\text{H}_{10}\text{Cl}_2\text{O}$: C, 49.80; H, 5.18; Cl, 36.80.

Found: C, 50.32; H, 5.47; Cl, 36.43.

Mol.wt. 190 (theory 193).

2,2-Dichloro-3-(1-propyl)cyclobutanone

A solution of 50.0 g. (0.22 mole) of freshly distilled trichloroacetyl bromide in 50 ml. of dry ether was added dropwise to a stirred mixture of 200 ml. of dry ether, 57.5 g. (0.88 mole) of zinc dust activated with copper, and 120 ml. (77.7 g.; 1.11 moles) of 1-pentene. At the conclusion of the exothermic reaction, the ether solution was separated from the unreacted zinc. The ether solution was extracted with 200 ml. of dry hexane, which resulted in the precipitation of the zinc halide. The solution was decanted, and the solvents were evaporated on a steam bath. The residue was distilled at reduced pressure to yield 8.0 g. of

2,2-dichloro-3-(1-propyl)cyclobutanone at 69.5-70.0° (1.5 mm). This corresponds to a 31 per cent yield.

Infrared absorption (smear): 1806 cm^{-1} (s).

Proton magnetic resonance: complex multiplet centered at 1.2 p.p.m. characteristic of the n-propyl group; complex multiplet centered at 3.0 p.p.m., which had an area that was 3/7 of the multiplet centered at 1.2 p.p.m.

Analysis: Calcd. for $C_7H_{10}Cl_2O$: C, 46.41; H, 5.52.

Found: C, 46.66; H, 5.65.

Mol. wt. 188 (theory 181).

Dichloroacetyl Bromide

The dichloroacetyl bromide was prepared from commercially available dichloroacetic acid and phosphorus tribromide. A 194 g. (1.5 moles) portion of dichloroacetic acid was placed in a 500 ml., one-necked flask equipped with a reflux condenser. A 175 ml. (500 g.; 1.87 moles) portion of phosphorus tribromide was added dropwise down the condenser. When the addition was complete, the reaction solution was heated at reflux for four hours. The crude dichloroacetyl bromide was distilled on a 30-plate Oldershaw column. There was obtained 216 g. (125-127°) of dichloroacetyl bromide which corresponds to a 75 per cent yield.

2,2-Dichloro-3-ethoxycyclobutanone

A solution of 200 ml. of dry ether, 70 ml. (53.3 g.; 0.74 mole) of ethyl vinyl ether, and 41 ml. (30 g.; 0.3 mole) of triethylamine was cooled to 0-5°C in an ice bath. To this solution was added dropwise with stirring a solution of 54 g.

(0.28 mole) of freshly distilled dichloroacetyl bromide in 50 ml. of dry ether. After the addition was complete, the reaction mixture was stirred for three hours. The triethylamine hydrobromide was removed by filtration, and the filtrate washed three times with water and dried over anhydrous magnesium sulfate. The solution was then filtered and the solvent removed by distillation. The residue was distilled at reduced pressure to yield 18.5 g. of 2,2-dichloro-3-ethoxycyclobutanone at 91-94° (2.5 mm). This corresponds to a 45 per cent yield.

Infrared absorption (smear): 1806 cm^{-1} (s).

Analysis: Calcd. for $\text{C}_6\text{H}_8\text{Cl}_2\text{O}_2$: C, 39.34; H, 4.37.

Found: C, 39.41; H, 4.64.

10,10-Dichlorobicyclo [6.2.0] dec-4-en-9-one

A solution of 200 ml. of dry hexane, 45.7 ml. (33.3 g.; 1.04 moles) of 1,5-cyclooctadiene was heated to reflux, and to the refluxing solution was added dropwise with stirring a solution of 50 g. (0.26 mole) of freshly distilled dichloroacetyl bromide in 50 ml. of dry hexane. After the addition was complete, the reaction mixture was heated at reflux for four hours. The amine salt was removed by filtration and the filtrate washed three times with water, and then dried over anhydrous magnesium sulfate. The solution was filtered and the solvent and excess olefin removed by

distillation. The residue was distilled at reduced pressure to yield 24.0 g. of 10,10-dichlorobicyclo [6.2.0] dec-4-en-9-one at 112° (1.0 mm). This corresponds to a 53 per cent yield.

Infrared absorption (smear): 1806 cm^{-1} (s); 1650 cm^{-1} .

Proton magnetic resonance: complex multiplet centered at 2.1 p.p.m. (methylene protons), multiplet centered at 3.4 p.p.m. and 5.0 p.p.m. (methinyl protons) and multiplet centered at 6.7 p.p.m. (vinyl protons). The peak areas were in the ratio of 8:1:1:2.

Analysis: Calcd. for $\text{C}_{10}\text{H}_{12}\text{Cl}_2\text{O}$: C, 54.79; H, 5.48.

Found: C, 55.0; H, 5.75.

2,2-Dichloro-3-phenylcyclobutanone

A solution of 77 g. (0.4 mole) of dichloroacetyl bromide in 50 ml. dry hexane was added with stirring to a refluxing solution of 200 ml. dry hexane, 61 ml. (45 g., 0.45 mole) of triethylamine, and 140 ml. (125 g., 1.2 moles) of styrene. The reaction mixture was heated at reflux for six hours and allowed to stand overnight at room temperature. The solution was filtered and the filtrate washed with water until the washings were neutral. The organic layer was removed and the solvent evaporated under nitrogen. The residue was distilled at reduced pressure to yield 13.0 g. of 2,2-dichloro-3-phenylcyclobutanone at 103° (1.6 mm). This corresponds to a 19 per cent yield.

Infrared absorption (smear): 1806 cm^{-1} .

Proton magnetic resonance: a multiplet centered at 7.2 p.p.m. (phenyl protons), a multiplet centered at 4.0 p.p.m. (methinyl proton) and a multiplet centered at 3.45 p.p.m. (methylene protons). These peak areas were in the ratio of 8:1:2.

Analysis: Calcd. for $\text{C}_{10}\text{H}_8\text{Cl}_2\text{O}$: C, 55.81; H, 3.72.

Found: C, 55.6; H, 3.53.

Attempted Preparation of 2,2-dichloro-3-cyanocyclobutanone

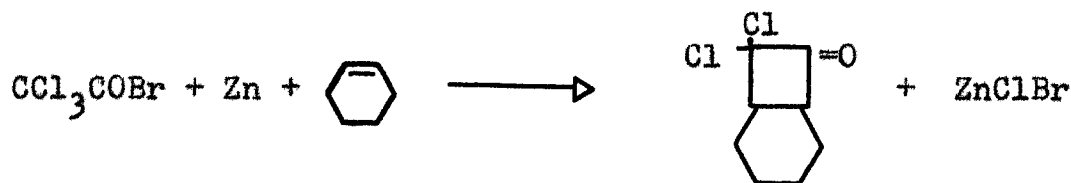
To a mixture of 200 ml. of dry hexane, 49 ml. (35.4 g.; 0.78 mole) of triethylamine, and 51.8 ml. (41.3 g.; 0.78 mole) of acrylonitrile was added dropwise with stirring to a solution of 77 g. (0.40 mole) of dichloroacetyl bromide in 50 ml. of dry hexane. After the addition was complete, the reaction mixture was stirred at room temperature for three hours. The triethylamine hydrobromide was removed by filtration, the filtrate washed three times with water, and then dried over anhydrous magnesium sulfate. The solution was filtered and the solvent and excess olefin were removed by distillation. The residue was distilled at reduced pressure to yield 1 g. of a liquid product. The infrared spectrum showed no characteristic cyclobutanone absorption.

CHAPTER III

DISCUSSION AND CONCLUSIONS

Dichloroketene has been prepared by the dehalogenation of trichloroacetyl bromide and also by the dehydrobromination of dichloroacetyl bromide. Due to the extreme reactivity of this new ketene, it is necessary to prepare this material and allow it to undergo cycloaddition in situ. This was the procedure followed in the cycloadditions investigated in this study.

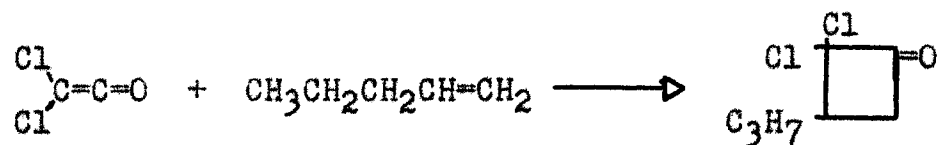
Cyclohexene was reacted in situ with dichloroketene, prepared by the dehalogenation of trichloroacetyl bromide, to yield 8,8-dichlorobicyclo [4.2.0] octan-7-one in 52 per cent yield.



Identification of the cycloadduct was based on elemental analysis and infrared and proton magnetic resonance spectra. An infrared band at 1806 cm^{-1} showed that the adduct was a substituted cyclobutanone. The proton magnetic resonance spectrum revealed the presence of methylene protons at 1.8 p.p.m. and two methinyl protons at 4.1 and 2.9 p.p.m.

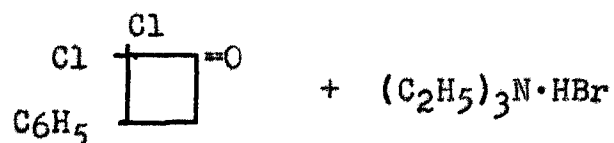
in the ratio of 8:1:1. This cycloadduct was also obtained from the generation of dichloroketene by dehydrohalogenation of dichloroacetyl bromide in the presence of cyclohexene.

The cycloadduct of dichloroketene and 1-pentene was obtained in 31 per cent yield by synthesizing the ketene by dehalogenation of trichloroacetyl bromide in the presence of the olefin.



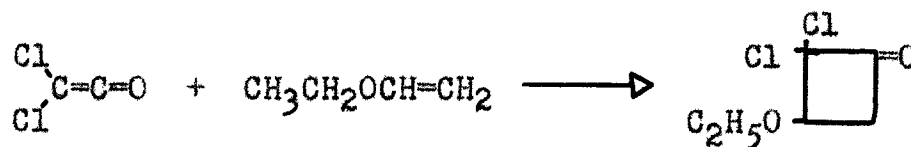
The structure of the cycloadduct, 2,2-dichloro-3-(1-propyl)-cyclobutanone, was proved by elemental analysis, infrared and proton magnetic resonance spectra. This cycloadduct could also be prepared by generating dichloroketene by the dehydrohalogenation method in situ with the olefin.

The cycloadduct of styrene and dichloroketene was obtained in 19 per cent yield. The ketene was generated by the dehydrobromination of dichloroacetyl bromide because styrene was polymerized in the dehalogenation system.



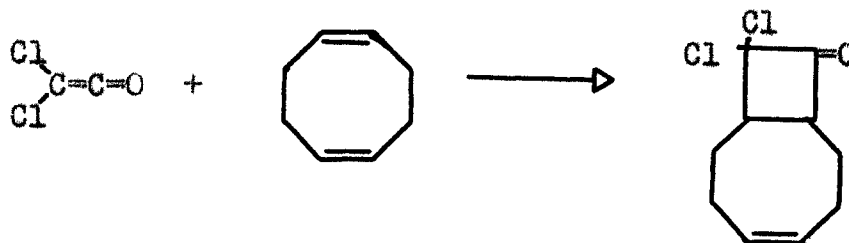
The proton magnetic spectrum showed a methylene group adjacent to a carbonyl group. The methylene groups adjacent to the carbonyl group in cyclobutanone occur at 3.03 p.p.m., while the remaining methylene group occurs at 1.96 p.p.m. (9). The methylene group in this styrene cycloadduct appeared at 3.45 p.p.m. No protons appeared in the 2 p.p.m. region where the β -protons of cyclobutanone absorb.

The dehydrobromination of dichloroacetyl bromide in the presence of ethyl vinyl ether produced 2,2-dichloro-3-ethoxycyclobutanone in 45 per cent yield.



The structural assignment was based upon elemental analysis and the infrared spectrum.

Dichloroketene, produced by the dehydrohalogenation method, underwent a 1,2-cycloaddition with 1,5-cyclooctadiene to produce 10,10-dichlorobicyclo [6.2.0] dec-4-en-9-one in 53 per cent yield.



The structure was assigned on the basis of infrared and proton magnetic resonance spectra and elemental analysis.


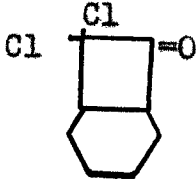
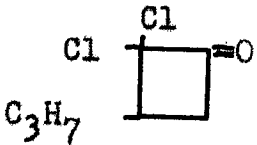
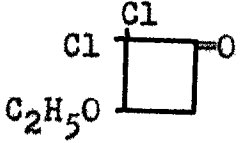
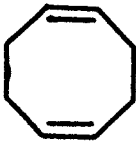
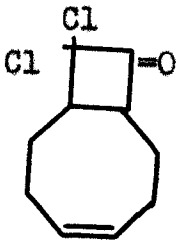
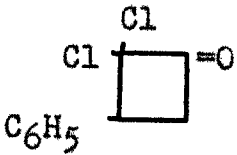
Numerous efforts were made to effect the cycloaddition of dichloroketene and acrylonitrile, a strongly electrophilic olefin, but no evidence of a cycloadduct was obtained. Consequently, this new ketene, like diphenylketene and dialkylketenes, will not undergo cycloaddition with strongly electrophilic olefins.

It is known that tertiary amine salts, which are by-products of the dehydrohalogenation reaction, catalyze the polymerization of ketenes (5, 6). This is particularly true for the lower molecular weight ketenes. Consequently, it was recognized that this undesirable polymerization would be a competing reaction and would be expected to lower the yields of cycloadducts. Although the dehalogenation system appears superior for the preparation of dichloroketene, this system is limited to the use of unactivated olefins, because Lewis acids, like the zinc halide produced in the reaction, are known to initiate the polymerization of activated olefins, such as ethyl vinyl ether and styrene. Therefore, the dehydrohalogenation method for the preparation of dichloroketene was primarily employed because nucleophilic, electrophilic, and unactivated olefins were studied and polymerization of the olefin presents no problem in this system.

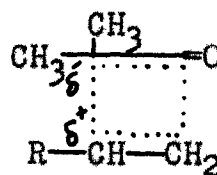
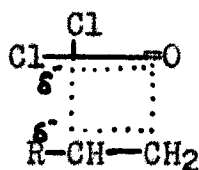
The successful cycloadditions of dichloroketene are summarized in Table I, page 18. Dichloroketene, unlike diphenylketene and dialkylketenes, undergoes cycloaddition with a variety of olefins, both activated and unactivated, with equal ease. The cycloaddition with the slightly electrophilic olefin, styrene, occurs with difficulty, as expected. In addition to the cycloadditions reported in this study, some cycloadditions of dichloroketene have recently appeared in the literature as indicated in the Introduction which are relative to the results of this investigation. Cyclopentadiene, a conjugated diene, reacts with dichloroketene to give the appropriate substituted cyclobutanone in 75 per cent yield (3, 7). Cyclopentene reacts with dichloroketene to give a substituted cyclobutanone in 67 per cent yield (3). It was also reported that indene and dichloroketene gave an adduct in 12 per cent yield (8).

Krapcho and Lesser recently reported a cycloaddition study with dimethylketene (4). The results indicate that dimethylketene forms 1,2-cycloadducts with olefinic substrates in good yields when reacted in situ at elevated temperatures. Dichloroketene appears to be somewhat more reactive than dimethylketene towards unactivated olefins since more vigorous conditions are required for the dimethylketene cycloadditions. Recent evidence in the

TABLE I
DICHLOROKETENE-OLEFIN ADDUCTS AND YIELDS

Olefin	Adduct	Yield
		52%
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$		31%
$\text{CH}_3\text{CH}_2\text{OCH}=\text{CH}_2$		45%
		53%
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$		19%
$\text{CH}_2=\text{CHCN}$	--	--

literature suggests that these cycloaddition reactions proceed by a near concerted process with some charge separation in the transition state (1, 2). If this is the case in these cycloaddition reactions, the following two proposed transition states might explain why dichloroketene is more reactive with unactivated olefins than dimethylketene. The chlorine atoms would be more effective in stabilizing the carbanionic character of the α -carbon atom and thus lower the energy requirements for the reaction.



Also, these transition states suggest that cycloaddition with a strongly electrophilic olefin (R is electron withdrawing) would be difficult because of the electron withdrawing substituent being attached to a carbon atom which possesses carbonium ion character.

In conclusion, this study suggests that dichloroketene is a valuable intermediate for the synthesis of a vast array of substituted cyclobutanones and while this ketene appears to be somewhat more reactive than diphenylketene and dialkylketenes with unactivated olefins, it is very similar in most respects.

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