

## Halogenated Ketenes. XXIII. 2-Oxetanones (1,2)

William T. Brady and Arvind D. Patel

Department of Chemistry, North Texas State University, Denton, Texas 76201

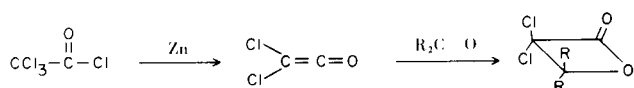
Received May 14, 1971

The cycloaddition of dichloroketene with several simple ketones to produce 2-oxetanones is described. The ketene is generated *in situ* by the zinc dehalogenation method and the zinc/zinc chloride activates the carbonyl group of the ketone. The cycloaddition of methylchloro- and methylbromoketenes with some activated carbonyl compounds is also described.

It has been recently reported that the cycloaddition of ketenes to carbonyl compounds to produce 2-oxetanones occurs readily when the carbonyl compounds are activated (3,4). Simple ketones which are not activated reportedly do not undergo cycloaddition. We have recently reported on the stereochemistry of the cycloaddition of some aldoketenes with chloral and found that both *cis*- and *trans*-2-oxetanones were produced in approximately equal amounts (5). During the course of that investigation, we found that the generation of dichloroketene by the zinc dehalogenation of trichloroacetyl chloride in the presence of acetone and cyclohexanone respectively, produced these 2-oxetanones. It was proposed that zinc was activating the carbonyl groups of the ketenes.

The purpose of this report is to describe a detailed study of the cycloaddition of dichloroketene with simple ketones in the presence of zinc and zinc chloride and to relate studies on the cycloaddition of methylchloro- and methylbromoketenes with activated carbonyl compounds.

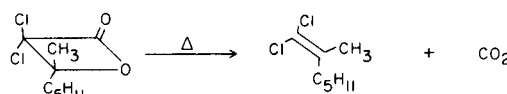
The generation of dichloroketene by the zinc dehalogenation of trichloroacetyl chloride in the presence of simple ketones resulted in the formation of the corresponding 2-oxetanones. These cycloadducts are illustrated in Table I.



Dichloroketene does not undergo cycloaddition with the simple ketones described when the ketene is prepared by the triethylamine dehydrochlorination of dichloroacetyl chloride. However, if zinc/zinc chloride are added to the dehydrohalogenation mixture, cycloaddition occurs. Unfortunately, this method cannot be used to effect the cycloaddition of dichloroketene and simple aldehydes. The aldehydes trimerize in the presence of the activated zinc and zinc chloride. Also, efforts to cycloadd dichloroketene

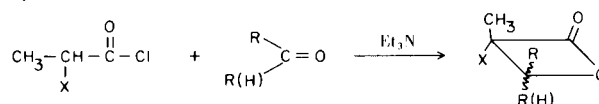
to crotonaldehyde, cinnamaldehyde and methyl vinyl ketone were unsuccessful.

2-Oxetanones are generally quite susceptible to decarboxylation to olefins when heated. The higher the boiling points of these cycloadducts the more this decarboxylation becomes significant. The cycloadduct of dichloroketene with methyl *n*-amyl ketone could not be isolated by vacuum distillation because decarboxylation occurred. However, the olefin was isolated and characterized.



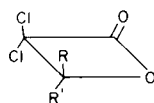
These dichloroketene cycloadditions are accompanied by the formation of an insoluble tar which is attributed to polymerization of the ketene. This is characteristic of reactions involving halogenated ketenes.

The cycloaddition of methylchloro- and methylbromoketenes with chloral, *o*-chlorobenzaldehyde and *sym*-dichlorotetrafluoroacetone was investigated and the results are shown in Table II. The ketenes were generated *in situ* by the triethylamine dehydrohalogenation of the  $\alpha$ -halo-propionyl halide. An examination of the carbonyl compounds in Table II reveals that activation of the carbonyl group is necessary for cycloaddition. This is substantiated by the fact that propionaldehyde, benzaldehyde, acetone and methyl ethyl ketone did not enter into cycloaddition with the methylhaloketenes under the conditions employed.



Cycloadditions of the methylhaloketenes with aldehydes and unsymmetrical ketones can produce *cis* and

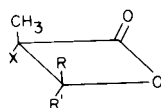
TABLE I  
2-Oxetanones from Dichloroketene-Ketone Cycloadditions (a)



R	R'	Yield (%)	B.p. C (mm)	Nmr, (b,c)	% Carbon		% Hydrogen	
					Calcd.	Found	Calcd.	Found
Me	Et	35	40 (0.5)	1.1 (t, 3H), 1.72 (s, 3H), 2.08 (q, 2H)	39.3	39.08	4.37	4.32
Me	<i>n</i> -Pr	35	53 (0.5)	1.1 (t, 3H), 1.78 (s, 3H), 1.5 (m, 2H), 2.0 (m, 2H)	42.6	42.67	5.07	4.96
Me	<i>i</i> -Pr	20	43 (0.5)	1.72 (s, 3H), 1.0 (d, 3H), 1.04 (d, 3H), 2.2 (m, 1H)	42.6	42.88	5.07	4.88
Me	CH <sub>2</sub> Cl	15	43 (0.5)	2.0 (s, 3H), 4.25 (s, 2H)	29.5	29.80	2.48	2.25
Me	CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	40	80 (d)	1.55 (s, 3H), 3.0 (d, 1H) 3.35 (d, 1H), 7.1 (s, 5H)	53.88	53.67	4.08	4.04
C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> Cl	20	125-130 (0.05)	4.25 (s, 2H), 7.18 (s, 5H)	45.2	45.02	2.65	2.43
CH <sub>2</sub> Cl	CH <sub>2</sub> Cl	23	85 (1.5)	3.9 (s)	25.2	25.54	1.68	1.65

(a) The dichloroketene cycloadducts with acetone and cyclohexanone have been reported (5). (b) Carbon tetrachloride solvent. (c) The infrared spectra revealed the carbonyl absorption at 1870-1885 cm<sup>-1</sup>. (d) M.p.

TABLE II  
2-Oxetanones from Methylhaloketene-Carbonyl Compound Cycloadditions



X	R	R'	Yield (%)	B.p. C (mm)	Nmr, (a,b)	% Carbon		% Hydrogen	
						Calcd.	Found	Calcd.	Found
Cl	CCl <sub>3</sub>	H	53	70 (0.5)	2.05 (s, 3H), 4.95 and 5.18 (2s, 1H)	25.21	25.53	1.67	1.51
Cl	<i>o</i> -ClPh	H	45	50 (0.2)	2.2 and 2.38 (2s, 3H), 6.35 and 6.45 (2s, 1H), 7.0 (m, 4H)	51.95	51.53	3.28	3.34
Cl	CF <sub>2</sub> Cl	CF <sub>2</sub> Cl	55	48-50 (1.5)	2.05 (s)	24.82	24.94	1.08	1.03
Br	CCl <sub>3</sub>	H	60	75-80 (0.4)	2.2 (s, 3H), 4.8 and 5.22 (2s, 1H)	21.27	21.26	1.42	1.65
Br	<i>o</i> -ClPh	H	50	125-30 (0.1)	2.1 and 2.27 (2s, 3H), 6.4 and 6.5 (2s, 1H), 7.0 (m, 4H)	43.6	44.13	2.93	3.34
Br	CF <sub>2</sub> Cl	CF <sub>2</sub> Cl	60	48-52 (0.5)	2.08 (s)	21.56	21.38	0.99	0.96

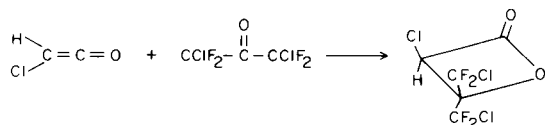
(a) Carbon tetrachloride. (b) The infrared spectra revealed the carbonyl absorptions at 1865-1900 cm<sup>-1</sup>.

*trans* isomers. Both *cis*- and *trans*-2-oxetanones were produced in these instances in approximately equal amounts as previously reported for the aldoketenes. The isomer distributions were determined by vapor phase chromatography and by nmr integration of the methinyl region.

The generation of ketenes by the triethylamine dehydrohalogenation method can present serious competing reactions; *e.g.*, reaction of the amine with the carbonyl compound. To alleviate this problem with *sym*-dichlorotetrafluoroacetone, a stoichiometric reaction of the amine

and the acid halide was effected at low temperature in the absence of the ketone, and then this reactant was added as the reaction mixture warmed to room temperature. Also, the order of addition of reagents is very important as the addition of triethylamine to the  $\alpha$ -halopropionyl halides resulted in the formation of  $\alpha$ -halovinyl esters of the acid halides (6). Furthermore, since triethylamine catalyzes the polymerization of chloral, these cycloadditions were accomplished by separate but simultaneous addition of the acid halide and amine to chloral in the solvent.

The dehydrohalogenation of chloroacetyl chloride in the presence of *sym*-dichlorotetrafluoroacetone resulted in the formation of the adduct derived from chloroketene.



### EXPERIMENTAL

Ether and hexane were dried over sodium immediately prior to use as solvents. All of the acid halides were commercially available except  $\alpha$ -halopropionyl chloride which was prepared from the corresponding acid and thionyl chloride. Chloral was vacuum distilled and used immediately. Zinc was activated as previously described (7).

Nuclear magnetic resonance (nmr) were recorded on a Jeolco Minimar 60 mHz or Jeolco NMR PS-100 mHz spectrometer.

#### Dichloroketene-Ketone Cycloadditions.

To a stirred mixture of 3 moles of activated zinc, 200 ml. of anhydrous ether and 2 moles of ketone was added dropwise an ether solution containing 1 mole of trichloroacetyl chloride at room temperature. Cooling of the reaction vessel was usually necessary and this was accomplished with an ice water bath. After the addition was complete, stirring was continued overnight. The excess zinc was removed by filtration and the filtrate concentrated and extracted with hexane to separate the oxetanone from the zinc chloride etherate and ketene polymer. The hexane extracts were combined, concentrated, and vacuum distilled to yield the 2-oxetanones.

#### Methylhaloketene Cycloadditions with Chloral.

A solution of 2 moles of freshly distilled chloral in 150 ml. of hexane was stirred while 1 mole of  $\alpha$ -halopropionyl chloride and 1.5 moles of triethylamine were added simultaneously at room temperature. The salt was removed by filtration and the filtrate concentrated. Distillation under reduced pressure afforded the 2-oxetanones.

#### Methylhaloketene Cycloadditions with *sym*-Dichlorotetrafluoroacetone.

A solution of 1 mole of triethylamine in 200 ml. of hexane was cooled to  $-78^\circ$  and then 1 mole of  $\alpha$ -halopropionyl chloride added dropwise. After the addition was complete, the reaction mixture was stirred at this temperature for 15-20 minutes and then 1.5 moles of *sym*-dichlorotetrafluoroacetone was added. After warming to room temperature, the salt was removed by filtration, the filtrate concentrated and the residue vacuum distilled to yield the 2-oxetanones.

#### Methylhaloketene Cycloadditions with *o*-Chlorobenzaldehyde.

A 1 mole portion of  $\alpha$ -halopropionyl chloride was added dropwise at room temperature to a stirred solution of 2 moles of triethylamine, 200 ml. of hexane and 1.5 moles of *o*-chlorobenzaldehyde. After the addition, stirring was continued at room temperature for 4 hours. The amine salt was filtered, the filtrate concentrated and the residue vacuum distilled to yield the 2-oxetanones.

#### 1,1-Dichloro-2-methyl-1-heptene.

The cycloadduct of dichloroketene and methyl *n*-amyl ketone was prepared by the general method indicated above. Prior to vacuum distillation, the residue revealed a band in the infrared spectrum at  $1870\text{ cm}^{-1}$  verifying the presence of the 2-oxetanone. However, upon distillation, decarboxylation occurred and the corresponding olefin was isolated in an overall yield of 40%; b.p.  $78-80^\circ$  (25 mm); ir,  $1635\text{ cm}^{-1}$ ; nmr (carbon tetrachloride),  $\delta$  0.8 (m, 3H), 1.3 (m, 6H), 1.85 (s, 3H), and 2.25 (m, 2H).

*Anal.* Calcd. for  $\text{C}_8\text{H}_{14}\text{Cl}_2$ : C, 53.3; H, 7.77. Found: C, 52.99; H, 7.57.

#### Cycloaddition of Chloroketene with *Sym*-Dichlorotetrafluoroacetone.

The same procedure was employed for this cycloaddition as described above for the methylhaloketenes with this ketone; (52%); b.p.  $45-47^\circ$  (1.5 mm); ir  $1895\text{ cm}^{-1}$ ; nmr (carbon tetrachloride),  $\delta$  5.52 (s).

*Anal.* Calcd. for  $\text{C}_5\text{HCl}_3\text{F}_4\text{O}_2$ : C, 21.81; H, 0.37. Found: C, 21.79; H, 0.69.

### REFERENCES

- (1) Support of this investigation by The Robert A. Welch Foundation, National Science Foundation and a North Texas State University Faculty Research Grant is gratefully acknowledged.
- (2) Paper XXII., W. T. Brady and J. P. Hieble, *J. Am. Chem. Soc.*, submitted.
- (3) D. Borrmann and R. Wegler, *Chem. Ber.*, **99**, 1245 (1966).
- (4) D. Borrmann and R. Wegler, *ibid.*, **102**, 64 (1969).
- (5) W. T. Brady and L. Smith, *J. Org. Chem.*, **36**, 1637 (1971).
- (6) W. T. Brady and F. H. Parry, III, R. Roe, Jr., E. F. Hoff, Jr., and L. Smith, *ibid.*, **35**, 1515 (1970).
- (7) W. T. Brady, H. G. Liddell, and W. L. Vaughn, *ibid.*, **31**, 626 (1966).