Phys. Org.

# Reactivity and Structure of Alkyl Vinyl Ethers. Part III.<sup>1</sup> Kinetics and Mechanism of Dichlorocarbene Addition Reactions

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The reaction of a series of alkyl vinyl ethers (ROCH=CH<sub>2</sub>) with dichlorocarbene (generated by reaction of potassium t-butoxide with chloroform) has been studied. Products were characterised as the appropriate dichlorocyclopropyl ethers. Competition experiments showed that the relative rates of reaction varied for a series of alkyl groups (R) in the order t-butyl (2·43), isopropyl (1·56), ethyl (1·20), methyl (1·03), isobutyl (1·00), 2-chloroethyl (0·48). On this scale, cyclohexene had a relative rate of 0·94. The order of reactivity is approximately parallel with that observed previously for acid-catalysed hydrolysis and it is suggested that the transition state for the carbene reaction involves the oxygen atom directly.

DICHLOROCARBENE reacts readily with many olefins to give the corresponding dichlorocyclopropane,<sup>2</sup> e.g.,

$$RCH = CH_2 + :CCI_2 \longrightarrow RCH - CH_2 (I)$$

Most carbene addition reactions in the liquid state occur at rates which approach collision frequencies and, in the case of appropriately substituted olefins, commonly lead to stereospecific addition products.<sup>2</sup> Consequently, it is not possible to measure absolute rates of such carbene reactions, but measurement of product composition, from reactions involving mixtures of olefins, has provided estimates of relative rate factors.<sup>3,4</sup> Relative rate studies were used by Doering,<sup>3</sup> Skell,<sup>4</sup> and their

<sup>1</sup> Part II, A. Ledwith and H. J. Woods, J. Chem. Soc. (B),

1966, 753. <sup>2</sup> A. Ledwith, "The Chemistry of Carbenes," R.I.C. Lecture Series Monographs, 1964, No. 5; J. Hine, "Bivalent Carbon," Ronald Press Co., New York, 1964; W. Kirmse, Carbene Chemistry, Academic Press, London, 1964.

collaborators in pioneering investigations of the reactivity of dichlorocarbene and dibromocarbene. These workers showed that dihalogenocarbenes reacted most readily with olefins containing electron-releasing substituents and should, therefore, be classified as electrophilic reagents. The only kinetic data for carbene reactions with alkyl vinyl ethers is that of Doering and Henderson<sup>3</sup> who reported the relative rate ratio for ethyl vinyl ether and cyclohexene = 1.86.

Vinyl alkyl ethers (ROCH=CH<sub>2</sub>) are excellent examples of electron-rich olefins and recent studies 1,5 of reactivity towards electrophilic reagents has shown that reaction rates are highly sensitive to the nature of the alkyl group (R) in the alkoxy-substituent. This effect is now shown to operate even in the reactions with the much less discriminating electrophile, dichlorocarbene.

<sup>3</sup> W. v. E. Doering and W. A. Henderson, jun., J. Amer. Chem. Soc., 1958, 80, 5274.

4 P. S. Skell and A. Y. Garner, J. Amer. Chem. Soc., 1956, 78, 5430. <sup>5</sup> D. M. Jones and N. F. Wood, J. Chem. Soc., 1964, 5400.

## EXPERIMENTAL

Materials.—Isopropyl and t-butyl vinyl ethers were presented by British Oxygen Company, Morden, Surrey. Isobutyl, ethyl, and  $\beta$ -chloroethyl vinyl ethers were commercial. All vinyl ethers were purified by washing 5 times with an equal volume of water (pH=8), dried (KOH, 24 hr.), decanted, and treated with fresh potassium hydroxide for a further 6 hr. and finally fractionally distilled through a packed column collecting the middle fraction (b. p.s: Bu<sup>t</sup>, 80·5—81·0°; Bu<sup>i</sup>, 83·1°; Pr<sup>i</sup>, 55·5—56·5°; Et, 35—35·5°;  $\beta$ -chloro-Et, 107·5—108°, all at 760 mm. Hg). Methyl vinyl ether (Matheson Company, Inc.) was distilled from the cylinder and collected at 0°. Cyclohexene (Hopkin and Williams) was distilled through an 18 in. packed column and the fraction of b. p. 82·5—83·0° collected.

Chloroform ('AnalaR') was washed three times with concentrated sulphuric acid, washed free from acid with

1011 cm.<sup>-1</sup>, and cyclopropane C-H stretch at 3073 cm.<sup>-1</sup> (Found: C, 45.7; H, 6.5. Calc. for  $C_7H_{12}Cl_2O$ : C, 45.9; H, 6.6%).

Performed in this manner (*i.e.*,  $CHCl_3$  added to base) the reaction always gave some tetrachloroethylene as byproduct and, depending on concentrations, the excess of base reacted with the dichlorocyclopropyl product.<sup>6</sup> Consequently for kinetic runs it was necessary to add base to chloroform.

The other derivatives were similarly synthesised. Their properties are summarised in Table 1, together with optimum operating conditions for characterisation by g.l.c.

Kinetic Measurement.—Although there are many methods of producing dichlorocarbene,<sup>2</sup> we used Doering and Henderson's procedure<sup>3</sup> (chloroform and potassium tbutoxide).

All reactions were carried out in a 100 ml. three-necked flask fitted with a calibrated dropping device and a reflux

TABLE 1
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Preparation and characterisation of dichlorocyclopropyl derivatives

Dichloro-	Yield			Operating temp. for g.l.c.			Carrier gas pressure	Retention
cyclopropane	(%)	В. р.	$d_{4}^{23}$	Injectors	Column	Detector	(lb./in.²)	time (sec.)
$C_3H_3Cl_2 \cdot OCH_3$	48	64·0-64·5° 77 mm.	1.198	170°	135°	145°	20	179
$C_3H_3Cl_2 \cdot OC_2H_5$	30	53—54 28 mm.	1.168	,,	,,	**	"	243
$C_3H_3Cl_2 \cdot OPr^i$	23	55 21 mm.	1.086	,,	,,	,,	,,	312
$C_3H_3Cl_2\cdot OBu^t$	33	79—80 21 mm.	1.118	**		**	,,	412
$C_3H_3Cl_2 \cdot OBu^i$	43	67 17 mm.	1.025	" 180	150 162	160 170	26	496 289 233
$C_3H_3Cl_2 \cdot O \cdot CH_2 \cdot CH_2Cl \dots$	47	92·593·5 4 mm,	1.305	,,	,,	,,	"	504
7,7-Dichloronorcarane	51	35 2 mm.	1.212	170	150	160	,,	522

water, dried (KOH, 24 hr.), and fractionally distilled, the fraction of b. p.  $60.5-61.5^{\circ}$  being collected and stored in the dark.

t-Butyl alcohol (Hopkin and Williams) was treated with potassium (2 g./l.) at  $35^{\circ}$  until the metal just dissolved. The dried alcohol was distilled and the fraction of b. p.  $82-83^{\circ}$  collected.

Potassium t-butoxide solution was prepared by dissolving potassium (2.03 g.) in t-butyl alcohol (500 ml.) at  $25^{\circ}$ .

Preparation and Characterisation of Reaction Products.— 1,1-Dichloro-2-isobutoxycyclopropane. Potassium (5 g., 0.13 mole) was added slowly to t-butyl alcohol (100 ml.) and allowed to dissolve. The excess of alcohol was distilled off and the residue dried at reduced pressure at 100° for 1 hr.

This residue was chilled in ice and isobutyl vinyl ether (20 g., 0.2 mole) in dried ether (50 ml.) added and stirred. To the resultant slurry chloroform (20 ml.) was added during **30** min. When addition was complete the mixture was stirred for 15 min. at 0°, then allowed to warm to room temperature. Ether (50 ml.) and water (50 ml.) were added, the layers separated, and the organic layer was further extracted with water (50 ml.), before being dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed and the product distilled at 67.5—69.0°/18 mm. (15.6 g., 43%). Redistillation gave pure 1,1-dichloro-2-isobutoxycyclopropane (12.0 g.), b. p. 67.0°/17 mm.,  $d_4^{25}$  1.025,  $n_p^{22.5}$  1.4120. The infrared spectrum showed C-Cl at 771 cm.<sup>-1</sup>, cyclopropane ring vibrations at

condenser; the third aperture was used for both temperature measurement and sampling.

In a typical run, equimolar amounts of the two vinyl compounds were pipetted into the flask, chloroform (10 ml.) added, and the mixture chilled to  $0^{\circ}$  in an ice-bath. The mixture was magnetically stirred.

A solution of potassium t-butoxide in t-butyl alcohol (5 ml.) was then added slowly so that the temperature did not rise above 5°. When addition was complete the mixture was stirred for a further 15 min. at low temperature before a sample (50  $\mu$ L) was taken and injected into the gas chromatograph to determine the proportion of the two dichlorocyclopropyl derivatives produced. The procedure was repeated for further additions of potassium t-butoxide.

The products of reactions were determined on an Aerograph Autoprep model 700 gas chromatograph fitted with a 10 ft.  $\times \frac{1}{8}$  in. column packed with 10% dinonyl phthalate on 60/80 Chromosorb P, with nitrogen as carrier gas. The injector, column, detector temperatures, and gas flow were adjusted to suit the pair of dichlorocyclopropyl compounds being determined (Table 1).

Injection of a series of standard volumes of the particular dichlorocyclopropyl derivative under the above conditions gave a linear response with peak area (vertical height  $\times$  half-height width) and plots of peak area against weight of

<sup>6</sup> J. Feeney, A. Ledwith, and L. H. Sutcliffe, J. Chem. Soc., 1962, 2021.

dichlorocyclopropane were straight lines passing through the origin. No internal standard was used as it was only necessary to determine the ratio of the two products in any sample being analysed.

#### RESULTS

Assuming that the addition of dichlorocarbene to an olefinic double bond is of the first order in both [:CCl<sub>2</sub>] and  $[R \cdot CH = CH_2]$ , then for reaction with two different olefins we have

$$d[A]/dt = k_1 [:CCl_2][R^1CH=CH_2]$$
(1)

$$d(B)/dt = k_2 [:CCl_2][R^2CH=CH_2]$$
(2)

where  $A = (I; R = R^1)$  and  $B = (I; R = R^2)$ In the present work  $[R^1 CH=CH_2]_0 = [R^2 CH=CH_2]_0$ , and

A series of such runs was performed with different pairs of vinyl ethers (and with cyclohexene) under similar conditions and the results are shown in Table 3. In all reactions the initial concentration of vinyl ether was 1.118M. Relative rates are shown in Table 4 and were self-consistent when measured from different combinations of olefins.

### DISCUSSION

Alkyl vinyl ethers have been shown to react readily with dichlorocarbene derived from potassium t-butoxide and chloroform. The nature of R in ROCH=CH<sub>2</sub> has a significant effect on the relative rates of dichlorocyclopropane formation as shown in Table 4, and this is surprising in view of the very high reactivity of carbene

## TABLE 2

Competitive reaction of isopropyl vinyl ether and t-butyl vinyl ether with dichlorocarbene in chloroform at  $0-5^{\circ}$ 

Initial 
$$[Pr^{i} OCH=CH_{2}] = [Bu^{t} OCH=CH_{2}] = 1.118M$$

 $[KOBu^t]$  in t-butyl alcohol = 0.109M

KOBu <sup>t</sup> soln. (ml.)	Isopropyl peak area (cm.²)	t-Butyl peak area (cm. <sup>2</sup> )	$10^9 \times (moles of isopropyl product)$	$10^9  imes$ (moles of t-butyl product)	$\frac{k_{\rm Bu}}{k_{\rm Pr}}$
5	1.25	1.18	0.835	1.28	1.53
10	1.74	1.69	1.15	1.83	1.59
15	2.68	2.49	1.79	2.68	1.50
20	3.11	3.02	2.07	3.31	1.60

\* In this case Bu is t-butyl and Pr is isopropyl; mean ratio 1.56.

[:CCl<sub>2</sub>] is the same for both olefins. Therefore, provided the extent of reaction is small, it is permissible to divide (1) by (2) and hence

$$[A]/[B] = k_1/k_2$$

By adding small increments of potassium t-butoxide solutions, *i.e.*,  $(:CCl_2)$  and determining the ratio of the products after each increment, a series of values of  $k_1/k_2$  was obtained from each run. A typical kinetic run is shown in Table 2.

TABLE 3

Relative reactivity dich	v of vinyl ethe lorocarbene	er pairs with
Vinyl ether (R in ROCH=	Mean value	
Α	в	$k_{\rm A}/k_{\rm B}$
$\operatorname{But}$	$\mathbf{Pr^{i}}$	1.56
Pr <sup>i</sup>	$Bu^i$	1.56
Et	$Pr^i$	0.77
Me	$\mathbf{Pr^{i}}$	0.66
Bu <sup>‡</sup>	Et	2.25
2-Chloroethyl	$\mathbf{Bu^{i}}$	0.48
(Cyclohexene)	$\mathbf{Bu^{i}}$	0.94
2-Chloroethyl (Cyclohexene)	Bu <sup>i</sup> Bu <sup>i</sup>	0.48 0.94

#### TABLE 4

### Relative reactivity of alkyl vinyl ethers (ROCH=CH<sub>2</sub>) towards electrophilic reagents

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R	CCl <sub>2</sub> a	H <sub>3</sub> O+ b	
But	$2 \cdot 43$	10.30	
Pr <sup>i</sup>	1.56	4.50	
Et	1.20	1.25	
Me	1.03	0.62	
Bu <sup>i</sup>	1.00	1.00	
Cl·CH <sub>2</sub> ·CH <sub>2</sub> ·	0.48	0.11	
(Cyclohexene)	0·94		

•  $KOBu^t + CHCl_3 + olefin$  mixture at  $0-5^\circ$ . • HCl in 80% aqueous acetone at  $25^{\circ}$  (ref. 1).

derivatives.<sup>2</sup> Reactivity of alkyl vinyl ethers towards electrophilic reagents results from resonance involving unshared electron pairs on oxygen, *i.e.*,

Previously it has been shown 1,5 that rates of acidcatalysed hydrolysis are extremely sensitive to the nature of R in the same series of alkyl vinyl ethers (Table 4). Relative rates of reaction with :CCl<sub>2</sub> are in roughly the same order as the rates of acid-catalysed hydrolysis although the scale is much compressed, as expected for the less discriminating reagent. In Part II<sup>1</sup> it was pointed out that the observed reactivity sequence, t-butyl > isopropyl > ethyl > methyl, was the reverse of the order of electron release to the double bond (as measured by n.m.r. techniques<sup>6</sup>) but agreed with the expected order of oxygen-atom basicity in the compounds.

The n.m.r. data related to the ground states of the alkyl vinyl ethers <sup>6</sup> and need not necessarily be reflected in the relative ease of transition state formation. However, by analogy with acid-catalysed hydrolysis, it is possible that the transition state for reaction of :CCl<sub>2</sub> with alkyl vinyl ethers involves a contribution from structures in which both oxygen atom and vinyl group are involved, e.g., as shown in Scheme 1. In any case, the very low reactivity of 2-chloroethyl vinyl ether cannot be fully accounted for by a simple inductive effect of the  $\beta$ chlorine atom on the vinyl group.

The relative rate ratio ethyl vinyl ether/cyclohexene = 1.28 observed in the present work differs significantly from the value of 1.86 reported by Doering and Henderson.<sup>3</sup> They employed reaction conditions involving



excess of base rather than excess of  $CHCl_3$ , as in the present work, and also employed somewhat lower temperatures. During the present investigation it was

established that the dihalogenocyclopropane products react readily with potassium t-butoxide <sup>7</sup> as in Scheme 2. Consequently, it is not meaningful to compare rate



data unless the precise reaction conditions are equivalent.

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<sup>7</sup> A. Ledwith and H. J. Woods, to be published.