THE RELATIVE REACTIVITY OF OLEFINS IN CYCLOADDITION WITH ZINC CARBENOID

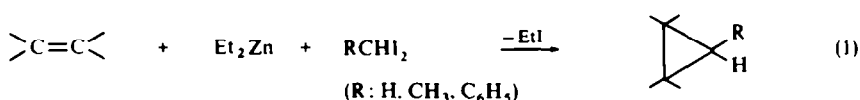J. Nishimura, J. Furukawa,* N. Kawabata,† and M. Kitayama

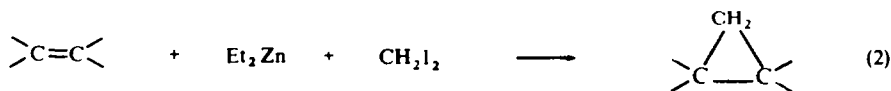Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan

Abstract--The relative reactivity of olefins was determined in the homogeneous reaction with zinc carbenoid generated from diethylzinc and CH_2I_2. The Hammett ρ-value for substituted styrenes in this reaction was -1.61. The inductive effect was concluded to be the most influential factor which determines the relative reactivity of olefins in the reaction. The mechanism of the reaction is discussed in comparison with other carbene and carbenoid reactions.

THE RELATIVE reactivity of olefins in the Simmons–Smith reaction has been studied by Blanchard *et al.*[1] and Rickborn *et al.*[2] According to these workers, the steric effect on the approach of zinc carbenoid to a carbon–carbon double bond is important in the reaction with tetraalkylethylene. On the other hand, Seyferth *et al.*[3] reported that the steric effect is not significant in the reaction of bis(bromomethyl)mercury with tetraalkylethylene although the reaction seemed to proceed through a transition state similar to that in the Simmons–Smith reaction. They ascribed the steric effect in the Simmons–Smith reaction to the coordination of ether to the zinc atom of the carbenoid. The present authors have reported the formation of zinc carbenoid in the reaction of diethylzinc and such gem-diiodoalkanes as CH_2I_2, ethylidene iodide and benzal iodide.[4]

$$\begin{array}{c}
{>}C{=}C{<} \quad + \quad Et_2Zn \quad + \quad RCHI_2 \quad \xrightarrow{\ -EtI\ } \quad \triangle\!\!<^R_H \qquad (1) \\[4pt]
(R: H. CH_3. C_6H_5)
\end{array}$$

The zinc carbenoids such as $EtZnCH_2I$ and $(ICH_2)_2Zn$ are assumed to be intermediates in reaction (2)[4e] and this may be closely related to that of the Simmons–Smith reaction.[4b] However, the Simmons–Smith reaction proceeds heterogeneously in the presence of zinc–copper couple whereas the reaction of the present authors is homogeneous. In this paper, the authors investigated the reactivity of olefins in cycloaddition reaction with the zinc carbenoid generated from diethylzinc and CH_2I_2.

$$\begin{array}{c}
{>}C{=}C{<} \quad + \quad Et_2Zn \quad + \quad CH_2I_2 \quad \longrightarrow \quad {>}C\!\!\overset{\displaystyle CH_2}{\underset{\textstyle \quad}{\diagup\!\!\diagdown}}\!\!C{<} \qquad (2)
\end{array}$$

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The relative reactivity of several olefins in reaction (2) was determined using cyclohexene as the standard. Table 1 summarizes the results with the relative reactivity of the olefins in other carbene and carbenoid reactions. The observed reactivity sequence of olefins in reaction (2) is in the order tetramethylethylene > trimethylethylene > cyclohexene > hept-1-ene in C_6H_6 and this order agrees with that of the nucleophilicity of olefins. Therefore, the inductive effect might predominate over the steric effect in reaction (2), because tetramethylethylene is most reactive among

TABLE 1. RELATIVE REACTIVITY OF OLEFINS

Olefin	k/k_c for reactant						
	RZnCH$_2$I						
	Et$_2$O[a]	n-Pentane[a]	Benzene[a]	Simmons–Smith procedure[b] Et$_2$O	(BrCH$_2$)$_2$Hg[c]	:CCl$_2$[d]	:CBr$_2$[c]
![tetramethylethylene]	8·82	16·2	12·5	1·27	26·9[f]	53·7	6·92
![trimethylethylene]	—	...	9·65	2·18	4·22[g]	23·4	7·41
![cyclohexene]	1·00	1·00	1·00	1·00	1·00	1·00	1·00
![hept-1-ene]	0·15	0·27	0·15	0·36	0·221	0·186	0·167

[a] Reaction conditions: Olefin, 20 mmole; Et$_2$Zn, 3 mmole; CH$_2$I$_2$, 2 mmole; solvent, 10 ml; 24·4 $\pm$ 0·1°C; 5 hrs.
[b] Ref. 1.
[c] Ref. 3.
[d] Ref. 11.
[e] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.* **78**, 5430 (1956).
[f] Relative reactivity of 2,3-dimethylpent-2-ene.
[g] Relative reactivity of 3-ethylpent-2-ene.

the olefins. On the other hand, it was found that the relative reactivity of tetramethylethylene in reaction (2) is slightly lower in ether than in C_6H_6 or n-pentane. This result seems to be ascribable to the steric effect caused by coordination of ether to the zinc atom of carbenoid, but the effect of ether is small compared with that assumed in the Simmons–Smith reaction. Therefore, the extremely low reactivity of tetraalkylethylene in the Simmons–Smith reaction is still obscure. Moreover, tetramethylethylene shows much higher reactivity than cyclohexene in reaction (2). The difference is much larger in reaction (2) than in the Simmons–Smith reaction.

The relative reactivity of unsaturated ethers in reaction (2) is given in Table 2 in

relation to the reactivity toward dichlorocarbene generated from CHCl$_3$ and potassium tert-butoxide.[5]

Table 2 shows that the zinc carbenoid in reaction (2) is more electrophilic than dichlorocarbene.

The relative reactivity of alkyl vinyl ether (ROCH=CH$_2$) in reaction (2) runs parallel to the electron-donating nature of the alkyl group.
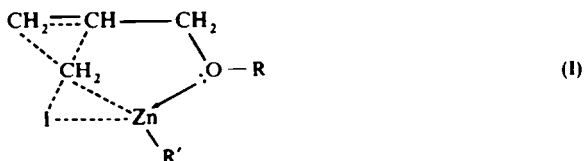
$$t\text{-Bu} > i\text{-Pr} > i\text{-Bu} > Et > ClCH_2CH_2 \quad (R \text{ in } ROCH=CH_2)$$

On the other hand, *cis*-alkenyl ethyl ethers (RCH=CHOC$_2$H$_5$) indicate a reverse order of reactivity with respect to the β-substituted alkyl group.

$$Me^* > Et \gtrsim i\text{-Pr} > H \quad (R \text{ in } cis\text{-RCH}=CHOC_2H_5)$$

In this case. it seems that the reactivity decreases with the order of bulkiness of the β-substituents, but *cis*-1-ethoxy-3-methylbut-1-ene (i-C$_3$H$_7$CH=CHOC$_2$H$_5$) having bulky isopropyl group as a β-substituent is more reactive than ethyl vinyl ether (CH$_2$=CHOC$_2$H$_5$). Consequently. the substituents have both electronic and steric effects in the reaction of olefins, and in reaction (2) the former effect (of β-substituent) is rather predominant over the latter.

In order to investigate the effect of ether oxygen, allyl i-butyl ether (CH$_2$=CHCH$_2$O-i-C$_4$H$_9$) and hept-1-ene (CH$_2$=CH(CH$_2$)$_4$CH$_3$) were compared and the former was found to be more reactive than the latter. The observation is contrary to the expectation according to polar substituent constants (Taft's σ*). In this case, the coordination of the allyl ether by means of oxygen atom to Zn atom of the carbenoid may stabilize the transition state (I), and enhance the reactivity of the allyl ether.[12]

The authors have already reported that reaction (2) with styrene accompanies polymerization but it is negligible if CH$_2$I$_2$/diethylzinc molar ratio is larger than three.[44]† The relative reactivity of substituted styrenes was investigated under the same conditions and the results are summarized in Table 3 in comparison with the relative reactivity with dichlorocarbene[6] generated from phenyl(bromodichloromethyl)-mercury.
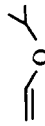
Logarithm of the relative reactivity of substituted styrenes in reaction (2) is plotted against Hammett σ-values in Fig 1. Fig 1 gives a ρ-value of -1.61 ± 0.05, which is larger than that in the reaction of phenyl(bromodichloromethyl)mercury with substituted styrenes.[6]
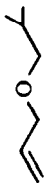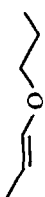
We have pointed out the importance of the inductive effect of the substituent of the olefins such as alkene, vinyl ether and alkenyl ether. The large ρ-value would also

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* *cis*-Propenyl n-propyl ether was used instead of *cis*-propenyl ethyl ether.

† The reaction with alkyl vinyl ether also accompanies polymerization besides the cycloaddition but the polymerization is negligible under normal reaction condition (CH$_2$I$_2$/diethylzinc ≤ 2).[44]

TABLE 2. RELATIVE REACTIVITY OF α,β-UNSATURATED ETHERS TOWARD ZINC CARBENOID AND DICHLOROCARBENE

Olefin	k/k_c for reactant	
	$RZnCH_2I^a$	$:CCl_2{}^b$
	3·09	2·43
	1·52	1·56
	0·36	1·20
	—	1·03
	1·00	1·00
	0·28	0·48
	0·18	0·94

1·43

0·28

2·98 (cis,)

1·98 (trans)

2·87 (cis)

1·07 (trans)

1·58 (cis)

[a] Reaction conditions: Olefin, 20 mmole; Et_3Zn, 3 mmole; CH_2I_2, 2 mmole; Et_2O as solvent, 10 ml; 24·4 ± 0·1°C; 5 hr.
[b] Ref. 5. The dichlorocarbene was generated from $CHCl_3$, and potassium t-butoxide.

TABLE 3. RELATIVE REACTIVITY OF SUBSTITUTED STYRENES IN REACTION (2) AND IN THE REACTION WITH $PhHgCCl_2Br$-INDUCED DICHLOROCARBENE

X/ρ		$RZnCH_2I^a$ $-1.61\,(\sigma)$	$PhHgCCl_2Br^b$ $-0.619\,(\sigma^+)$
	p-CH_3	1.64	1.52
	H	1.00	1.00
k/k_c	p-F	0.681	0.961
	p-Cl	0.464	0.839
	m-CF_3	0.175	0.453

^{a} Reaction conditions: Olefin, 10 mmole; CH_2I_2, 10 mmole; Et_2Zn, 3 mmole; C_6H_6 as solvent, 10 ml; 78.6 ± 0.1 °C; 15 hr.
^{b} Ref. 6.

suggest the importance of the inductive effect of the substituent. In other words, the methylene transfer (II) by $RZnCH_2I$ is a more nucleophilic reaction than that (III) of the dichlorocarbene.

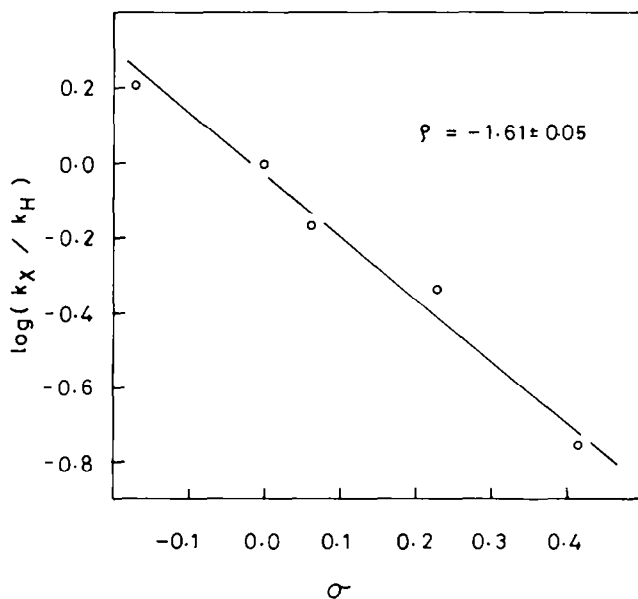

FIG 1. THE HAMMETT CORRELATION OF RELATIVE REACTIVITY OF SUBSTITUTED STYRENES IN REACTION (2).

EXPERIMENTAL

Analyses were performed at the Elemental Analysis Center of Kyoto University. NMR spectra were recorded on a Japan Electron Optics Lab. Model C6OH Spectrometer, using CCl_4 as solvent and TMS as internal standard. VPC were obtained with a Shimazu GC-2C gas chromatograph and Hitachi–Perkin-Elmer gas chromatograph F6-D having a capillary column. All reactions were carried out under an atmosphere of dry N_2. All b.p.s. are uncorrected.

Diethylzinc and CH_2I_2 were purified as described in previous papers.[4] 2-Methylbut-2-ene, 2,3-dimethylbut-2-ene,[7] cyclohexene, t-butyl vinyl ether,[8] i-propyl vinyl ether,[8] p-methylstyrene, p-fluorostyrene, p-chlorostyrene, and m-trifluoromethylstyrene[9] were prepared by conventional methods. Alkenyl ethers were prepared by the reported route[10] and fractionally distilled with a spinning band column. Other reagents were commercial materials and distilled before use.

Preparation of tri- and tetramethylcyclopropanes and cyclopropyl ethers. Low boiling cyclopropane derivatives were prepared as the following example. 2-Methylbut-2-ene (0·04 mole, 2·8 g), diethylzinc (0·04 mole, 4 ml), and CH_2I_2 (0·08 mole, 6·4 ml) were allowed to react in toluene (20 ml). After stirring at room temperature for 5 hr, the reaction mixture was directly distilled with a packed column. First fraction (52–53°C) was the desired trimethylcyclopropanes. Yield was almost quantitative. Physical properties of new cyclopropane derivatives are as follows:
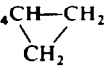
t-Butyl cyclopropyl ether bp 102°C, n_D^{25} 1·4033; Found: C 73·80; H, 12·63; Calcd.: C, 73·63; H, 12·36%.
i-Propyl cyclopropyl ether bp 87°C, n_D^{25} 1·3959; NMR (τ, CCl_4): m 9·35–9·70(4H); d 8·85 (6H, $J = 6·6$ Hz); m 6·50–7·00 (1H); sept. 6·35 (1H, $J = 6·6$ Hz).
2-Chloroethyl cyclopropyl ether bp 131°C, n_D^{25} 1·4372; Found: C, 49·54; H, 7·56; Cl, 29·20; Calcd: C, 49·81; H, 7·52; Cl, 29·40%.

Preparation of arylcyclopropanes. Substituted styrene (0·10 mole), diethylzinc (0·15 mole, 15 ml) and CH_2I_2 (0·20 mole, 16 ml) were allowed to react in C_6H_6 (50 ml) at 80°C for 10 hr. Results are summarized in Table 4.

TABLE 4. SUBSTITUTED PHENYLCYCLOPROPANES PREPARED BY REACTION (2) WITH SUBSTITUTED STYRENES[a]

$XC_6H_4CH—CH_2$ $\diagdown \diagup$ CH_2	Yield (%)	Bp (lit.) °C/mmHg	n_D^{25} (lit.)
p-CH_3	67	50–52/6 (194–4·5/745)[b]	1·5254 (1·5246 (20°))[b]
H	77	89–94/50 (64–65/20)[c]	1·5307 (1·5307)[c]
p-F	23	43/10 (90/45)[d]	1·5057 (1·5051)[d]
p-Cl	16	62–68/6 (110–15/15)[e]	1·5480 (1·5508 (20°))[e]
m-CF_3[f]	6	57/15	1·4630

[a] Reaction conditions: $XC_6H_4CH=CH_2$, 0·10 mol; $ZnEt_2$, 0·15 mol; CH_2I_2, 0·20 mol; C_6H_6, 20 ml; 80°C; 8–30 hr.
[b] V. K. Potapov, Yu. S. Shabarov and R. Ya. Levina, *Zh. Obsch. Khim.* **34**, 2512 (1964).
[c] Ref. 4b.
[d] R. G. Pews, *J. Am. Chem. Soc.* **89**, 5605 (1967).
[e] J. Smejkal, J. Jonas and J. Farkas, *Collection Czech. Chem. Commun.* **29**, 2950 (1964).
[f] Found: C. 64·88; H, 5·01; F, 30·14; Calcd.: C, 64·51; H, 4·87; F, 30·61%.

Competitive reactions. In a dry 50 ml three-necked flask, equipped with a magnetic stirring bar, a dropping funnel and a reflux condenser topped with a N_2 inlet tube, were charged with cyclohexene (12·5 mmole, 1·0274 g), tetramethylethylene (8·30 mmole, 0·6986 g), and 5 ml of 0·6 M C_6H_6 soln of diethylzinc, and 5 ml of 0·4 M C_6H_6 soln of CH_2I_2 was placed in a dropping funnel under N_2. The flask was set in a large water bath whose temperature was regulated to 24·4 ± 0·1°C. The solution of CH_2I_2 was added dropwise with stirring. After 5 hr, the mixture was treated with 20 ml of NH_4Claq and washed with H_2O. The organic layer was dried over $MgSO_4$ and analyzed directly by VPC. Competitive reactions for other olefins and vinyl ethers were carried out in a similar manner.
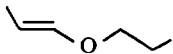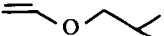
The competitive reaction for substituted styrenes was carried out in a sealed tube as the following example. A 40 ml dried reaction tube was charged with 5 ml of 0·6 M C_6H_6 soln of diethylzinc, styrene (5·72 mmole. 0·5955 g), p-chlorostyrene (5·55 mmole, 0·7687 g). CH_2I_2 (9·55 mmole, 2·5586 g). and 5 ml of C_6H_6 under N_2. The sealed tube was set in a large water bath whose temperature was regulated to 78·6 ± 0·1°C. After shaking 70 times per min for 15 hr, the reaction mixture was treated as mentioned above.

The relative reactivity was calculated by the following equation;[11]

$$k_X/k_Y = (P_X/P_Y)(O_Y/O_X)$$

where P is the mole of product, and O is that of reactant. The quasi-first order kinetics with respect to reactants was ascertained in each reactions as is shown in Table 5.

TABLE 5. COMPETITIVE REACTIONS OF TWO KINDS OF OLEFINS WITH VARIED MOLAR RATIO

A	B	A/B	k_A/k_B	Av.
	a	0·475	1·95	
		0·648	2·11	
		0·974	1·95	1·98
		1·042	1·91	
		1·234	1·97	
p-ClC$_6$H$_4$CH=CH$_2$	C$_6$H$_5$CH=CH$_2$ b	0·834	0·426	
		0·970	0·494	
		1·350	0·494	0·464
		2·381	0·441	

a Reaction conditions: Olefin, 20 mmole; CH_2I_2, 2 mmole; Et_2Zn, 3 mmole; Et_2O, 10 ml; 24·4 ± 0·1°C; 5 hr.

b Reaction conditions: Olefin, 10 mmole; CH_2I_2, 10 mmole; Et_2Zn, 3 mmole; C_6H_6, 10 ml; 78·6 ± 0·1°C; 15 hr.

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