Tetrahedron Letters No.4, pp. 263-265, 1968. Pergamon Press. Printed in Great Britain.

THE CHEMISTRY OF CUMULATED DOUBLE BOND COMPOUNDS VII
THE REACTION OF DIPHENYLKETENE WITH OXAZIRANES

Yoshiki Ohshiro, Toru Minami, Kiyoshi Yasuda and Toshio Agawa

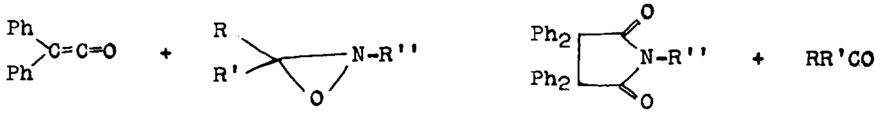
Faculty of Engineering, Osaka University, Yamada-Kami, Suita, Japan.

(Received in Japan 12 November 1968; received in UK for publication 13 December 1968)

It has been reported that the cycloaddition proceeded in the reaction of the heterocumulene with the three-membered heterocyclic compound comprising one hetero atom (1-3). On the other hand, there is no information regarding a reaction between a heterocumulene and a three-membered heterocyclic compound comprising two hetero atoms.

The object of this paper was to clarify the structure of the product and the mechanism in the reaction of diphenylketene with oxazirane.

It was found that N-substituted tetraphenylsuccinimide was obtained in the reaction.



(I~III)

Reaction conditions and results were shown in Table I.

TABLE I

No.	oxazirane R	R'	R''	reaction temp. °C	reaction time hr.	yield of imide %	m.p. °C	
1	Ph	H	CH_3	60	0.5	26	131-131.5	I
2	Ph	H	n-C_4H_9	60	0.5	50	125-126	II
3	Ph	H	c-C_6H_{11}	80	1.0	30	208	III
4	Ph	CH_3	n-C_4H_9	60	0.5	88	125-126	I
5	C_2H_5	CH_3	n-C_4H_9	60	0.5	38	125-126	I

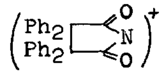
Oxazirane was added into benzene solution of diphenylketene with stirring at such a rate that the temperature did not rise above 60-80°C. Ketone or aldehyde, which was identified by IR and GLC, was removed by the distillation, and the product (N-substituted tetraphenyl succinimide) was isolated by column chromatography (Al_2O_3-benzene).

In the reaction in which the leaving group from oxazirane is aldehyde or dialkylketone yields of imide were not so high (No. 1,2,3,5). On the contrary the yield was relatively high in the reaction in which the leaving group was arylketone (No. 4). Any effect of C-substituent of oxazirane ring was not observed for the structure of the main product. The structures of N-substituted tetraphenyl succinimides were confirmed by IR, nmr, mass spectrometry and the elemental analysis.

For N-n-butyl tetraphenyl succinimide (II), following data were obtained.

IR : 1670 and 1740 cm^{-1} (C=O)

nmr : 2.8τ(Ph-), 6.9τ(CH_2-N), 8.8τ($-C_2H_4-$), 9.3τ($-CH_3$)

mass spectrum : m/e 459 (parent ion), m/e 402 , m/e 332 (Ph_2C-CPh_2)$^+$

(The calculated molecular weight of II is 459).

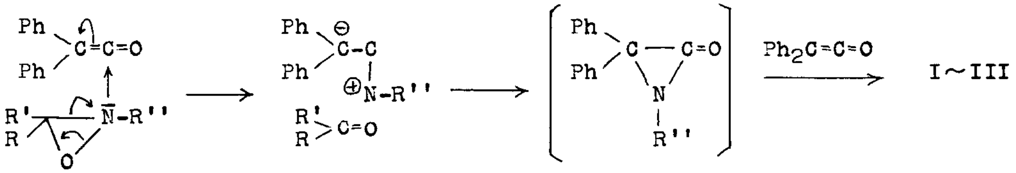
For another products (I, III) similar agreements were obtained. Results of elemental analysis of I, II and III were shown in Table II.

TABLE II

	found			calculated		
	C %	H %	N %	C %	H %	N %
I	83.39	5.31	3.33	83.43	5.55	3.36
II	83.63	6.38	3.04	83.63	6.36	3.05
III	84.58	6.29	2.85	84.09	6.43	2.88

It is reasonable to consider the reaction mechanism as follows. The lone pair electron of nitrogen of oxazirane attacks the center carbon of ketene group, α-lactam (IV) is formed by the release of aldehyde or ketone, α-lactam reacts immediately with ketene, and then succinimide derivative is obtained.

α-Lactam cannot be isolated because of the unstability.



(IV)

Oxaziranes were prepared by Emmons's method (4), an oxidation of corresponding imine with perbenzoic acid, and active oxygen was determined by the iodometry (Table III).

TABLE III

No.	R	R	R''	b.p. °C/mmHg	yield %	active oxygen %
1	Ph	H	CH_3	74-76/9	60	70
2	Ph	H	$n-C_4H_9$	90/1.5	72	94
3	Ph	H	$c-C_6H_{11}$	90/0.2	50	90
4	Ph	CH_3	$n-C_4H_9$	60/0.4	61	84
5	C_2H_5	CH_3	$n-C_4H_9$	76/60	-	74

REFERENCES

1) K. Gulbins, Ber., 94, 3287 (1961).
2) Y. Ohshiro et al, Tetrahedron Letters, in press.
3) E. Gublbins, R. Morlock, Ann., 698, 180 (1966).
4) W. D. Emmons, J. Am. Chem. Soc., 79, 5739 (1957).