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Electronic State of Ethoxycarbonylnitrene Generated by α-Elimination under Two-phase Conditions

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The base decomposition of ethyl *p*-nitrophenylsulfonyloxycarbamate in organic-aqueous two-phase systems in the presence of *cis*- or *trans*-4-methyl-2-pentene and quaternary ammonium or phosphonium halides afforded both stereospecific and nonstereospecific addition products of ethoxycarbonylnitrene. The electronic state of the nitrene was analyzed on the basis of Skell's hypothesis.

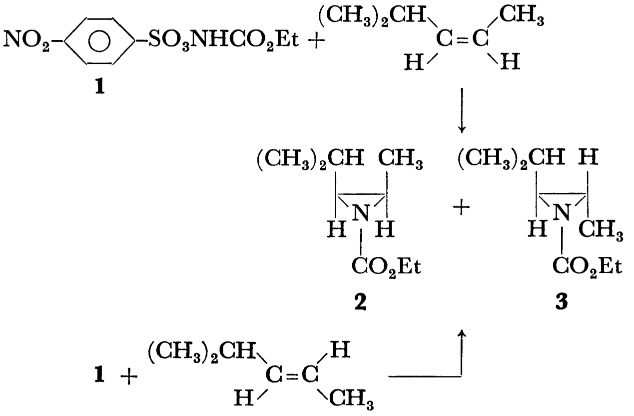
In the previous paper,[1)] we reported that ethoxycarbonylnitrene was generated by α-elimination reaction of ethyl *p*-nitrophenylsulfonyloxycarbamate (**1**) and reacted with cyclohexene in organic-aqueous two-phase systems in the presence of phase transfer catalysts. In these reactions the variation of reaction path through singlet or triplet nitrene was shown as the dependence of addition/insertion product ratio on the concentration of cyclohexene.

In the present study the electronic state of ethoxycarbonylnitrene generated under two-phase conditions is examined by analyzing the composition of the reaction products with *cis*- or *trans*-4-methyl-2-pentene on the basis of Skell's hypothesis.[2)]

Results and Discussion

Table 1 shows the yield of aziridines and the fraction of nonstereospecific addition (inversion) products in the reaction with *cis*- and *trans*-4-methyl-2-pentene under two-phase conditions (Scheme 1). No significant differences were observed in the catalysis of ammonium chlorides and bromides, but ammonium iodides gave unusual results; that is, the yields of addition product are low and the fractions of nonstereospecific addition product are decreased.

The ethoxycarbonylnitrene generated by α-elimination is supposed to be a singlet nitrene, which adds stereospecifically to olefins with complete retention of configuration.



Scheme 1.

Since the ground state of the nitrene is triplet, a part of the singlet nitrene decays to the triplet nitrene, which adds nonstereospecifically to olefins. As a side reaction, ethyl carbamate is formed by hydrogen abstraction reaction from the triplet nitrene. The reaction scheme is summarized in Fig. 1.

When triethylbenzylammonium chloride (TEBACl) was used as a phase transfer catalyst, the relationship between the concentration of *cis*- or *trans*-4-methyl-2-

Table 1. Reaction of ethyl *p*-nitrophenylsulfonyloxycarbamate (**1**) with *cis*- and *trans*-4-methyl-2-pentenes[a)]

Catalyst	From *cis*-olefin		From *trans*-olefin	
	% Yield of aziridine	% Fraction of *trans*-product	% Yield of aziridine	% Fraction of *cis*-product
$(CH_3)_4NBr$	0	0	0	0
$(C_2H_5)_4NBr$	11.4	59.3	5.2	17.6
$(n\text{-}C_4H_9)_4NBr$	19.8	41.9	17.8	14.8
$(n\text{-}C_4H_9)_4PBr$	16.6	46.5	13.7	13.9
$(n\text{-}C_4H_9)_4NI$	6.3	15.3	5.3	11.8
$n\text{-}C_8H_{17}N(C_2H_5)_3Br$	25.6	38.0	20.2	20.3
$n\text{-}C_{12}H_{25}N(C_2H_5)_3Br$	27.0	46.0	20.9	14.2
$n\text{-}C_{16}H_{33}N(C_2H_5)_3Br$	29.0	42.4	23.9	18.3
$n\text{-}C_{16}H_{33}N(CH_3)_3Br$	22.2	48.2	16.5	15.5
$(C_6H_5CH_2)N(C_2H_5)_3Cl$	26.7	38.2	24.9	17.3
$(C_6H_5CH_2)N(C_2H_5)_3Br$	34.3	35.3	28.3	19.4
$(C_6H_5CH_2)N(C_2H_5)_3I$	11.3	10.0	4.7	6.4

a) **1** 0.01 mol, olefin 0.02 mol, catalyst 1.0 mmol, CH_2Cl_2 40 ml, $NaHCO_3$ 0.03 mol, H_2O 30 ml, room temperature, 2 h.

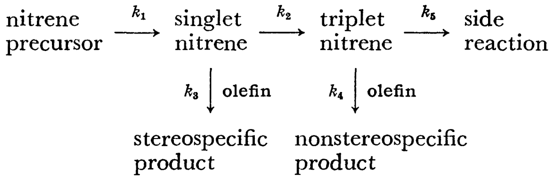


Fig. 1. Reaction scheme.

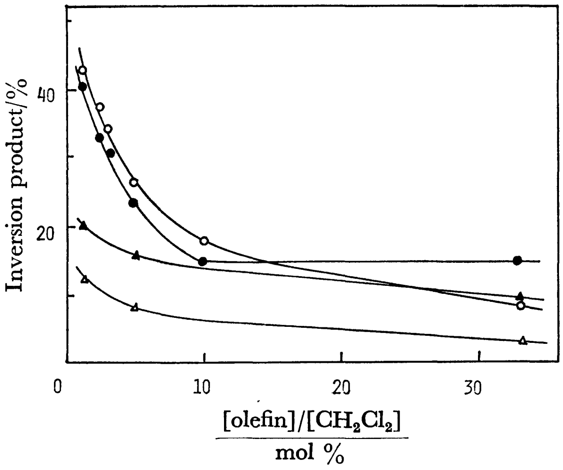


Fig. 2. Addition of ethoxycarbonylnitrene to *cis*- and *trans*-4-methyl-2-pentene under two-phase conditions in the presence of TEBACl.

●; *cis*-4-Methyl-2-pentene under two-phase conditions, ▲; *trans*-4-methyl-2-pentene under two-phase conditions, ○; *cis*-4-methyl-2-pentene in the homogeneous system,[3] △; *trans*-4-methyl-2-pentene in the homogeneous system.[3]

pentene in dichloromethane and the fraction of inversion product is shown in Fig. 2. In comparison with the results for the homogeneous system investigated by Lwowski *et al.*,[3] which are also shown in Fig. 2, the portion of the inversion product of the reaction with *cis*-4-methyl-2-pentene under two-phase conditions is a little low, while that of the reaction with *trans*-4-methyl-2-pentene is a little high, but concerning the dependence on the olefin concentration, the same trend is found for both the homogeneous and the two-phase systems. Thus, the increase in the concentration of olefin leads to a descrease in the inversion product. This can be explained as a consequence of an increasing frequency of the singlet nitrene reaction at higher concentrations of the olefins.

Now we consider the electronic state of the ethoxycarbonylnitrene generated in the present system according to the method proposed by Lwowski *et al.*[3,4] The fraction of the aziridine produced from the triplet nitrene in the total aziridine obtained is designated $[T]$, and the fraction of the "*trans*-aziridine" **3** in the aziridine produced from the triplet nitrene is designated α. If one assumes that the composition of the aziridine mixture produced from the triplet nitrene depends on the position of the equilibrium of the two conformers of open-chain biradical intermediate and not on the nature of the starting olefin, the fraction A of **3** in the aziridine mixture obtained from the *cis*-olefin and the fraction B of the "*cis*-aziridine" **2** in the aziridine mixture obtained from the *trans*-olefin are expressed respectively as;

$$A = [T]\alpha, \quad B = [T](1-\alpha) \qquad (1)$$

The following relation is derived from Eq. 1.

$$\alpha = A/(A+B) \qquad (2)$$

In order to know the value of A/B from the experimental data, the difference in the reactivity of *cis*- and *trans*-olefins toward the nitrene should be taken into consideration. From the measurements on the homogeneous system by Lwowski *et al.*,[3] the ratio of the reactivity $k_{4,trans}$: $k_{4,cis}$ is determined to be 0.7. This value is affected by the nature of olefin, but not affected by the nature of nitrene. Then, we can adopt this value for the present systems and then we can obtain the value of A/B from the experimental data shown in Fig. 2, by comparing the value of A at a given concentration with the value of B at 1/0.7 of that concentration. The values of A/B thus obtained vary from 1.5 to 2.1 in the concentration range from 33 to 1.5 mol %. The average value of A/B is 1.8, and the value of α is determined to be 0.64 from Eq. 2.

When the fraction of the aziridine produced from the singlet nitrene in the total aziridine is denoted as $[S]$, we get from Eq. 1

$$[T] = 1.56A, \quad [S] = 1 - [T] \qquad (3)$$

From the reaction scheme shown in Fig. 1, the following relation is obtained by assuming the stationary state with respect to the triplet nitrene,

$$\frac{[T]}{[S]} = \frac{k_2}{k_3\{[\text{olefin}]+(k_5/k_4)\}} \qquad (4)$$

Then, a plot of $[T]/[S]$ *vs.* $1/\{[\text{olefin}]+(k_5/k_4)\}$ should give a strainght line having the slope of k_2/k_3. Various plots were drawn by assuming various values of k_5/k_4 and the value of k_5/k_4 which gives the best straight line was determined. The selected value of k_5/k_4 for the two-phase reaction with TEBACl is 0.005, and then

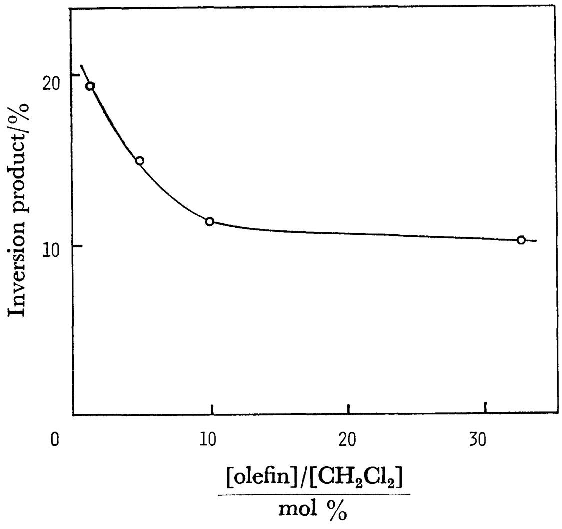


Fig. 3. Addition of ethoxycarbonylnitrene to *cis*-4-methyl-2-pentene under two-phase conditions in the presence of TEBAI.

the value of k_2/k_3 is determined to be 0.033 from the slope of the line.

When triethylbenzylammonium iodide (TEBAI) is used as a phase transfer catalyst, the relationship between the concentration of *cis*-4-methyl-2-pentene in dichloromethane and the inversion product is shown in Fig. 3. According to the same procedure as the case of TEBACl, the values of k_5/k_4 and k_2/k_3 were determined to be 0.07 and 0.033, respectively.

Table 2. Rate constant ratios k_2/k_3 and k_5/k_4 of the reactions of ethoxycarbonylnitrene under various conditions

	Two-phase system		Homogeneous system	
	TEBACl	TEBAI	α-Elimination with triethylamine[a)]	Thermolysis of ethyl azidoformate[b)]
k_2/k_3	0.033	0.033	0.036	0.10
k_5/k_4	0.005	0.07	0.015	0.03

a) From Ref. 4. b) From Ref. 3.

Table 2 summarizes the values of k_2/k_3 and k_5/k_4. The results of the two-phase reactions using TEBACl or TEBAI as phase transfer catalysts are compared with those of α-elimination reaction by triethylamine in a homogeneous system[3)] and the thermolysis of ethyl azidoformate.[4)] It is revealed from these results that the singlet nitrenes generated in the two-phase system and in the homogeneous system have the similar reactivity and the addition reaction of the singlet nitrene is about 30 times faster than the decay to the triplet state. However, there is a difference in the reactivity of the triplet nitrene. In the case of TEBACl, the ratio of side reactions such as hydrogen abstraction to form ethyl carbamate is low compared with the case of homogeneous system, while the ratio of side reactions (k_5/k_4) is very high in the case of TEBAI. Iodide ions from the catalyst is considered to enter into the organic phase easier than chloride or bromide ions, and the results imply that triplet nitrene is consumed by iodide ions in some unknown processes.

Experimental

The materials used and the authentic samples of the aziridines are described in the previous paper.[1)] The reactions of ethyl *p*-nitrophenylsulfonyloxycarbamate (**1**) with *cis*- or *trans*-4-methyl-2-pentene were carried out in dichloromethane solutions and aqueous sodium hydrogencarbonate solutions in the presence of phase transfer catalysts. The details of the reactions and the analyses of the products are also described in the previous paper.[1)]

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