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INSERTION OF ETHOXYCARBONYLNITRENE TOWARD *AXIAL* AND *EQUATORIAL* C-H BONDS

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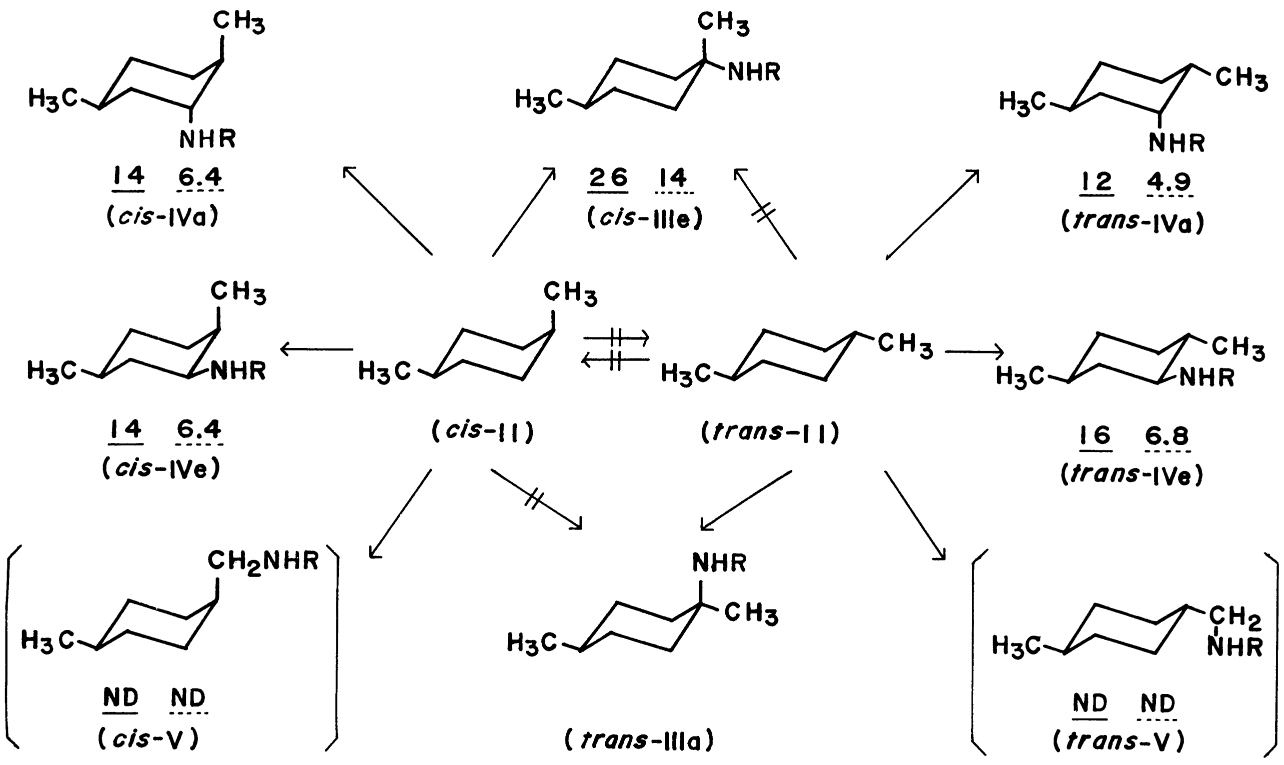
Ethyl azidoformate was decomposed on heating or by irradiation with UV in *trans*- and *cis*-1,4-dimethylcyclohexanes. Relative reactivities of the nitrene insertion toward *axial* and *equatorial* C-H bonds were calculated from the results. It was found that the reactivities toward *axial* C-H bonds were less than those of *equatorial* C-H bonds.

Ethoxycarbonylnitrene,1) generated by thermal or photochemical decomposition of ethyl azidoformate and by α-elimination of *N*-*p*-nitrobenzenesulfonoxyurethane, can insert into various types of C-H bonds, such as primary, secondary, tertiary,2,3) *endo*, *exo*,4) bridge and bridgehead4,5) C-H bonds, showing different reactivities. We wish to report the insertion reactivities of the nitrene toward *axial* and *equatorial* C-H bonds.

In thermal decomposition, a solution of ethyl azidoformate (I, 0.025 mole) in *cis*-1,4-dimethylcyclohexane (*cis*-II, bp 124°C, mp −87°C, 0.5 mole)6) was refluxed until no more evolution of nitrogen was observed. In the same manner, the reaction of I with *trans*-II (bp 119°C, mp −37°C)6) was carried out. In photochemical decomposition, a solution of I (0.05 mole) and II (0.25 mole) in dichloromethane (0.75 mole, to prevent freezing of *trans*-II) was irradiated by a low pressure mercury vapor arc (mainly 2537 Å) on stirring at a dry ice methanol temperature. The products were separated and collected vapor phase chromatographically, and the yield of each product was determined by VPC, using an internal standardization method.7) The structure of the products was established by their elemental analyses, and IR and NMR spectrography.

The products and their yields are displayed in Scheme 1. The values with solid and dotted underlines show mol % yields (based on I used) in thermolysis and photolysis, respectively. The insertion products (V) toward the methyl C-H bonds of II were not detected, even if the products were present, their yields might be trace because of less reactivity of the nitrene into primary C-H bonds.2,3) No interconversion between *cis*-II and *trans*-II was observed under either thermal or photolytic conditions. Neither formation of *trans*-IIIa from *cis*-II nor that of *cis*-IIIe from *trans*-II was observed by VPC. This stereospecific insertion of ethoxycarbonylnitrene toward C-H bond was recognized also in the reaction of the nitrene with optically active 3-methylhexane.8)

Scheme I



R : $-COOC_2H_5$ ND : not detected

Dividing the insertion yields toward secondary C-H bonds (IVa + IVe) and those toward tertiary C-H bonds (III) by the number of hydrogen atoms of secondary and tertiary C-H bonds, respectively, insertion yield toward each C-H bond is obtained. Thus, the relative reactivities of tertiary C-H bond to secondary C-H bond are estimated, although *axial* and *equatorial* bonds are not distinguished (3° C-H/2° C-H in Table 1). The 3° C-H/2° C-H ratios for *cis*-II are larger than those for *trans*-II in both cases of thermolyses and photolyses. The result represents a difference of insertion reactivities between *axial* and *equatorial* C-H bonds, because two tertiary C-H bonds of *trans*-II are occupied exclusively at *axial* positions, whereas,

Table 1 Insertion Reactivities of Ethoxycarbonylnitrene toward *axial* and *equatorial* C-H Bonds

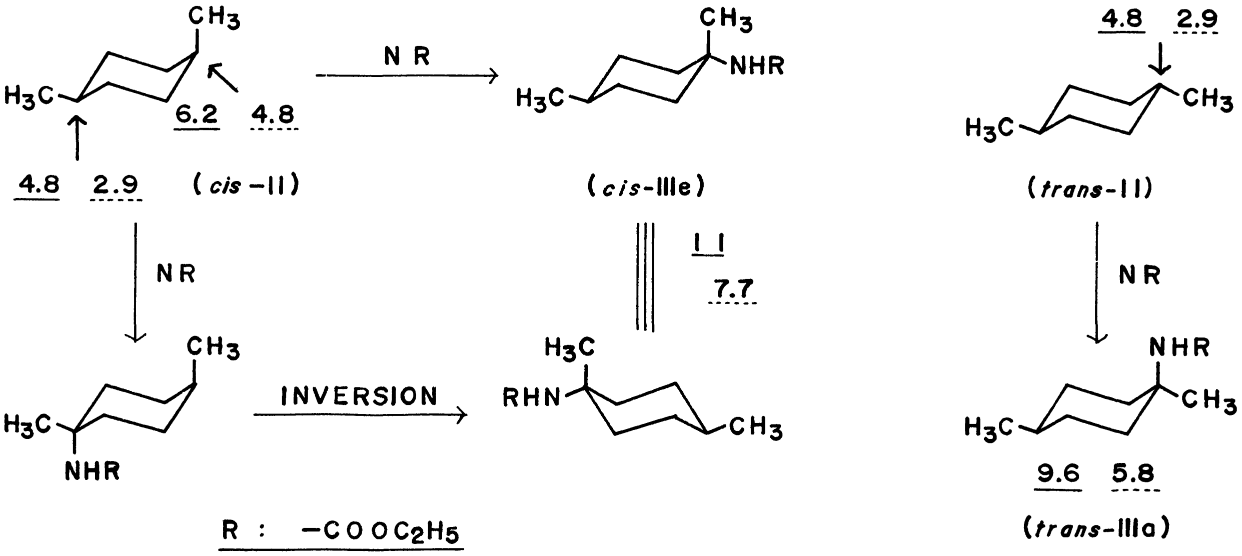
Relative reactivity		$\frac{3^\circ \text{ C-H}}{2^\circ \text{ C-H}}$	$\frac{2^\circ \text{ C-H}\underline{\text{e}}}{2^\circ \text{ C-H}\underline{\text{a}}}$	$\frac{3^\circ \text{ C-H}\underline{\text{e}}}{3^\circ \text{ C-H}\underline{\text{a}}}$
Thermolysis	*cis*-II	3.7		1.3
	trans-II	3.1	1.3	
Photolysis	*cis*-II	4.3		1.7
	trans-II	3.7	1.4	

one tertiary C-H bond of *cis*-II is occupied at *axial* position and another one is at *equatorial* position.

The relative reactivity of *equatorial* C-H bond to *axial* C-H bond (2° C-H*e*/2° C-H*a*) is obtained from the reaction of I with *trans*-II . The ratios of product yields, *trans*-IVe/*trans*-IVa, represent the relative reactivities of the *equatorial* secondary C-H bond to the *axial* C-H bond. In the reaction with *cis*-II , however, *cis*-IVa is a product derived from the insertion into either *equatorial* secondary C-H bond or *axial* C-H bond, because *cis*-II has a flexible form, and so with *cis*-IVe. The 2° C-H*e*/2° C-H*a* ratios, 1.3 in the thermolysis and 1.4 in the photolysis (Table 1), are close upon the C-H*exo*/C-H*endo* ratio of 1.6 for norbornane.4)

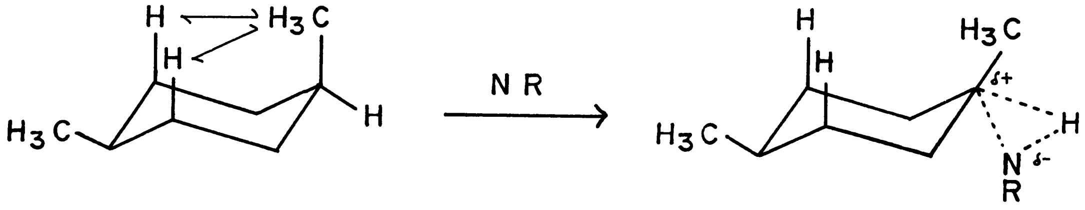
With regard to the reactivity of tertiary C-H bond, a comparison between the reactivities of the *axial* and *equatorial* bonds has been made based on the results of the following competitive reaction. The thermal and photochemical decompositions of ethyl azidoformate were carried out in a mixture of equimolecular amounts of *cis*-II and *trans*-II . The results are displayed in Scheme 2. In the case of thermal decomposition, the yield for insertion toward one *axial* tertiary C-H bond is given to be of 4.8 mole % from the yield (9.6 mole %) of *trans*-IIIa. Then, the insertion yield for the *axial* tertiary C-H bond and that for the *equatorial* tertiary C-H bond of *cis*-II are estimated to be of 4.8 and 6.2 mole %, respectively, from the yield (11 mole %) of *cis*-IIIe. In the case of photochemical decomposition also, the yields for each tertiary C-H bond were calculated in the same manner. The relative reactivities toward C-H bonds are summarized in Table 1 (3° C-H*e*/3° C-H*a*).

Scheme 2



As shown in Table 1, the axial C-H bond is somewhat less reactive than the equatorial C-H bond for the insertion of the nitrene. Axial positions are in a more crowded environment than equatorial positions and this gives rise to differences in reactivities between the two types of C-H bonds. On the other hand, considering that the steric requirements of the transition state, in general, are greater than those of the ground state, the insertion toward C-H bond at the equatorial position permits the axial methyl group at that position to move away from the strained (by γ-opposing effect) axial comformation[9] in the angular transition state[1] (Scheme 3). This decrease in steric strain should make the insertion toward equatorial C-H bond easier.

Scheme 3



R : $-COOC_2H_5$

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