662 © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *662—666 (1983)* [Vol. 56, No. 3

The Reactions of the Singlet NH Radicals with C_4 Olefins in the Liquid Phase

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(Received May 1, 1982)

The reactions of NH radicals with C_4 olefins, *trans-* and *cis*-2-butenes, 1-butene, and isobutene, were investigated by the photolysis of hydrogen azide in the liquid olefin at 0 °C and at the temperature of Dry Ice–methanol. Except for nitrogen and ammonia, amines and aziridines were found to be formed in good yield. 2-Butene-1-amine and *trans*-2,3-dimethylaziridine from *trans*-2-butene, 2-butene-1-amine and *cis*-2,3-dimethylaziridine from *cis*-2-butene, 3-butene-1- and 2-amines and 2-ethylaziridine from 1-butene, and 2-methyl-2-propene-1-amine and 2,2-dimethylaziridine from isobutene. These product formations were successfully explained by the insertion into the C–H bond and the addition to the double bond of olefin by the singlet NH radicals. In the case of 2-butene, no isomerized aziridine formation was observed. This result suggested that the triplet NH radicals rarely add to the double bond of olefin.

The reactions of NH radicals with lower olefins, ethylene and propene, have been reported.[1,2] The formations of aziridine and amine were explained by the addition and the insertion reactions of the singlet NH radicals, NH($a^1\Delta$), which were formed by the photolysis of hydrogen azide. The mechanism and the nature of the intermediate of these reactions have not yet been established. Amines are likely formed in an insertive attack of the NH singlet on the C–H bond of olefins as with paraffin.[3–7] For the aziridine formation, the following possibilities should be considered: (a) a concerted addition of the singlet NH radicals to the double bond of olefin, (b) an addition of the singlet NH radicals to the C atom of the double bond to form a singlet biradical, which is followed by the ring closure, and (c) a triplet biradical formation by the addition of the NH triplet, NH($X^3\Sigma^-$), followed by the spin inversion and ring closure. Aziridine formed by (a) process should retain the conformation of reactant; that is, cis isomer formation from cis olefin and trans isomer formation from trans olefin. Cis and trans isomer formations are expected from (b) and (c) processes, although the cis and trans ratio may depend on the nature of the biradicals and the experimental conditions.

The insertion and the addition reactions of O and CH_2, which are isoelectronic species of NH, have been extensively investigated.[8,9] In the reactions of methylene with 2-butene, it is well known that the singlet species add to the double bond of an olefin while they retain the stereospecificity, and the triplet species add without retaining stereospecificity.[10,11] Although O(^1D) adds to 2-butene while retaining the conformation of reactant,[12] O(^3P) gives *cis* and *trans* epoxide simultaneously. The cis and trans isomer ratio depended on the reaction temperature and/or the phase.[13,14]

In the previous paper,[1] the aziridine formation by the NH triplet was ignored in order to explain the concentration dependence of the ammonia formation. This explanation was based on the assumption that ammonia is formed by a hydrogen-atom abstraction from hydrogen azide. If ammonia is formed by the reactions of the NH singlet with olefin, the reaction of the NH triplet with olefin has to be included in the mechanism. If this is the case, both *cis-* and *trans*-aziridine formations may be expected in the reactions with *cis-* or *trans*-2-butene.

To continue such studies, we examined the photolyses of hydrogen azide in liquid *cis-* and *trans*-2-butenes, 1-butene, and isobutene at 0 °C and at the temperature of Dry Ice–methanol.

Experimental

The experimental methods and the apparatus used were essentially the same as those described in the previous paper.[1] Hydrogen azide was prepared and purified by the method already described.[1] Pure grade *trans-* and *cis*-2-butenes, 1-butene, and isobutene (Takachiho Shoji Co.) were used after having been distilled at a low temperature under vacuum. The mixture of hydrogen azide and olefin was prepared in a quartz tube (8 mm o.d.) or Pyrex tube (8 mm o.d.). The hydrogen azide solution was irradiated with a medium pressure mercury lamp (Wako Denki Co.) at 0 °C or at the temperature of Dry Ice–methanol. In the case of the quartz tube, a filter (Toshiba UV 27) was used to eliminate the light of wavelengths shorter than 250 nm.

After the irradiation, non-condensable products at −196 °C were analyzed with a combination of a Toepler pump, a gas buret, and a CuO furnace at 300 °C. The solvent hydrocarbon was evacuated at a temperature lower than −80 °C. Less volatile products, including unreacted hydrogen azide, were passed through a trap packed with NaOH coated glass wool, in order to decompose the quarternary ammonium salts which eventually formed.[4] The products thus obtained were analyzed with GLC, using a column packed with Amipack 124 (Gasukuro Kogyo Co., 3 m in length at 60 °C). Since authentic samples for the all products were not available, the sensitivity of an unavailable product i (S_i) was estimated from its retention time (Rt_i) using the relation: $S_i = a\,Rt_i + b$. The constants a and b were estimated using available amines and aziridines. Since the relation holds well for the amines and aziridines examined, the sensitivities, thus estimated, may be correct within an error of 30%.

The identification of the products was mainly done by the comparisons of their relative retention times and their mass spectra. The GC-mass spectrometer (Nichiden Varian, TE 600) was used. An NMR spectrometer (Varian, EM 390) was also used, using D_2O as a solvent.

Results

The photolyses of hydrogen azide in the liquid *cis*- and *trans*-2-butenes, 1-butene, and isobutene were examined at 0 °C or at the temperature of Dry Ice–methanol. In every case examined, nitrogen and ammonia were found to be formed, much as in the cases of ethylene and propene.[1)] Neither methane nor hydrogen was detected. The less volatile products were subjected to the analysis by GLC after having been treated with NaOH. The results obtained are summarized as follows:

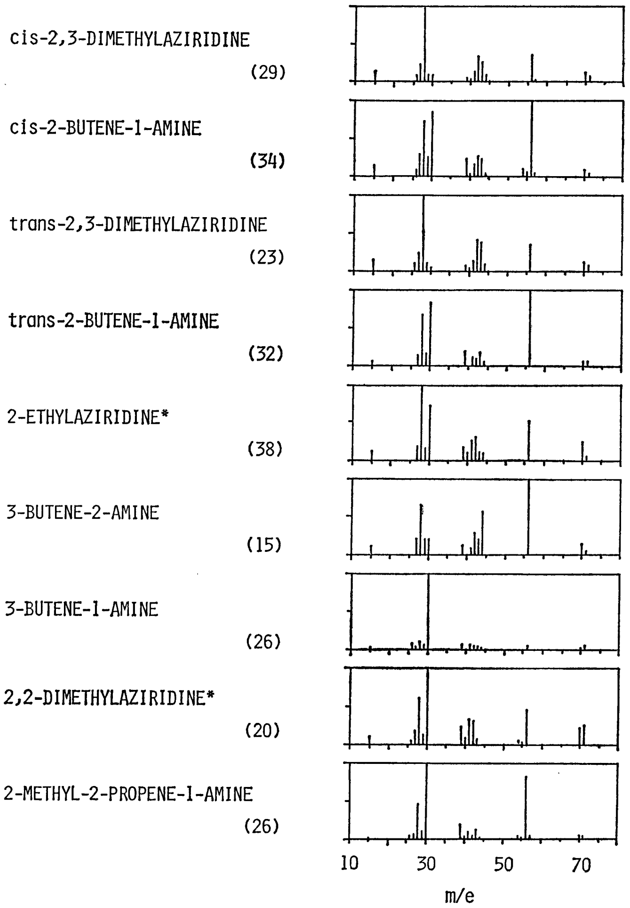

Fig. 1. The mass spectra of the products obtained in the photolyses of hydrogen azide in the liquid *cis*- and *trans*-2-butenes, 1-butene, and isobutene. The values in the parentheses show the retention times (see Text). The mass spectrum of the compound with an asterisk could be compared with that reported.[18)]. The abscissa shows the mass number.

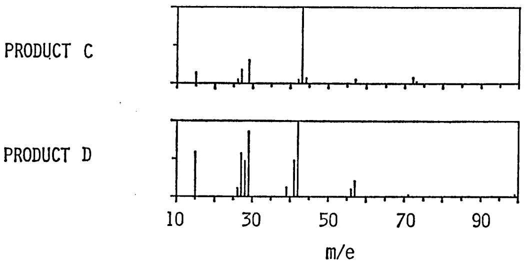

Fig. 2. The mass spectra of the products eluted at 22 min (product C) and 43 min (product D). For the detail, see Text. The abscissa shows the mass number.

cis-*2-Butene*. In the case of *cis*-2-butene, 6 peaks were separated by GLC using a column of Amipack 124. Their retention times were 5, 15, 22, 29, 34, and 43 min. The main two peaks, which eluted at 29 and 34 min, were identified to be 2,3-dimethylaziridine and 2-butene-1-amine from the mass spectra shown in Fig. 1. The configuration of the aziridine was assigned to be cis isomer on the basis of its NMR spectrum, NMR(D_2O) δ 1.0 (3H, d, CH_3) and 2.1 (1H, m, CH), by the comparison with the reported values for *cis*- and *trans*-2,3-dimethylaziridine.[15)] The mass spectra of the minor products eluted at 22 and 43 min are shown in Fig. 2. The 43 min product was tentatively assigned to be *s*-butyl azide. The product of 22 min could not be identified. The mass spectrum is apparently different from that of the product of 23 min obtained in the reaction of *trans*-2-butene. The product of 5 min was identified to be ethanamine by the comparison with the mass spectrum obtained using an authentic sample. The product eluted at 15 min gave the same mass spectrum as was obtained in the case of 1-butene (see later).

The yields of these products relative to that of nitrogen are shown in Table 1. The relative yields of the products were almost constant for the changes in the concentration of hydrogen azide and the irradiation time, except for ethanamine and *s*-butyl azide. The relative yield of ethanamine increased with an increase in the irradiation time. This trend suggested that this product was formed by the secondary reactions.

trans-*2-Butene*. In the case of *trans*-2-butene, 5 peaks were observed on the gas chromatogram. Their retention times were 5, 15, 23, 32, and 43 min. The main products eluted at 23 and 32 min were identified to be 2,3-dimethylaziridine and 2-butene-1-amine from their mass spectra shown in Fig. 1. The *cis-trans* configuration of the aziridine, NMR(D_2O) δ 1.0 (3H, d, CH_3) and 1.7 (1H, m, CH), was assigned to be in trans form by comparison with the reported values.[15)] 2-Butene-1-amine formed from *trans*-2-butene, NMR(D_2O) δ 1.7 (3H, d, CH_3), 3.3 (2H, d, CH_2), and 5.6 (m), eluted at 32 min, while the amine formed from *cis*-2-butene, NMR(D_2O) δ 1.6 (3H, d, CH_3), 3.2 (2H, d, CH_2), and 5.6 (m), eluted at 34 min. It is hard to assign the *cis-trans* configuration from the mass and NMR spectra. Since only one isomer could be obtained, the former was tentatively assigned to be in trans form and the latter to be in cis form. The products eluted at 5, 15, and 43 min were the same as those obtained in the case of *cis*-2-butene. The large peak of *trans*-2,3-dimethylaziridine probably masked the small peak eluted at 22 min obtained in the case of *cis*-2-butene; therefore, the amount of *trans*-2,3-dimethylaziridine was corrected by assuming that the relative yield of the product at 22 min is the same as that obtained in the case of *cis*-2-butene. No *cis*-2,3-dimethylaziridine formation was observed. Table 2 shows the relative yields of products obtained at the various concentrations of hydrogen azide, irradia-

Table 1. The yields of products relative to that of nitrogen obtained in the photolysis of hydrogen azide in the liquid *cis*-2-butene at 0 °C[a]

$[HN_3]$ mmol dm^{-3}	IT[b] min	NH_3	*c*DMA (29)	*c*2B1A (34)	A (5)	B (15)	C (22)	D (43)
42	30	0.24	0.32	0.16	0.01	0.04	0.07	0
42	60	0.22	0.32	0.18	0.02	0.04	0.06	0
42	90	0.23	0.28	0.21	0.02	0.04	0.05	0
83	30	0.27	0.36	0.21	0.02	0.05	0.09	0.03
82	60	0.25	0.30	0.21	0.02	0.04	0.08	0.03
82	90	0.28	0.21	0.22	0.03	0.04	0.05	0.02
156	30	0.23	0.29	0.22	0.02	0.04	0.07	0.04
156	60	0.25	0.24	0.25	0.03	0.04	0.06	0.07
	Average	0.25 ±0.02	0.29 ±0.05	0.21 ±0.03		0.04 ±0.01	0.07 ±0.01	

a) A Pyrex cell was used. The abbreviations of products are *c*DMA = *cis*-2,3-dimethylaziridine and *c*2B1A = *cis*-2-butene-1-amine. A, B, and D were tentatively identified to be ethanamine, 3-butene-2-amine, and *s*-butyl azide respectively. For details, see Text. The values in the parentheses show the retention times of the products. b) IT = Irradiation time.

Table 2. The yields of products relative to that of nitrogen obtained in the photolysis of hydrogen azide in the liquid *trans*-2-butene[a]

$[HN_3]$ mmol dm^{-3}	IT[b] min	NH_3	*t*DMA (23)	*t*2B1A (32)	A (5)	B (15)	D (43)
41	30	0.20	0.38	0.16	0.01	0.04	0.03
42	60	0.21	0.33	0.16	0.02	0.04	0.02
42	90	0.20	0.33	0.19	0.02	0.04	0.02
83	30	—	0.25	0.15	0.02	0.04	0.04
81	60	0.25	0.30	0.18	0.03	0.03	0.04
81	90	0.29	0.30	0.27	0.04	0.04	0.04
84[c]	30	0.17	0.37	0.22	0.02	0.04	0.05
84[c]	60	0.18	0.33	0.21	0.04	0.04	0.06
99	60	0.27	0.32	0.26	0.04	0.04	0.06
150	60	0.24	0.24	0.24	0.05	0.04	0.18
211	90	0.25	—	0.25	0.05	—	0.16
211	150	0.27	—	0.24	0.06	0.03	0.09
	Average	0.23 ±0.04	0.31 ±0.05	0.21 ±0.04		0.04 ±0.01	

a) A Pyrex cell was used. The abbreviations of the products are *t*DMA = *trans*-2,3-dimethylaziridine and *t*2B1A = *trans*-2-butene-1-amine. A, B, and D are the same as shown in Table 1. Reaction temperature was 0 °C except indicated. The values in the parentheses show the retention times of the products. b) IT = Irradiation time. c) Reactions at the temperature of Dry Ice–methanol.

tion times, and the reaction temperatures. Much as in the case of *cis*-2-butene, the relative yields of the products were almost constant, except for ethanamine and *s*-butyl azide.

1-Butene. In the case of 1-butene, 6 peaks were separated on the gas chromatogram at 5, 15, 22, 26, 38, and 60 min. The main products eluted at 15, 26, and 38 min were identified to be 3-butene-2- and 1-amines and 2-ethylaziridine. The mass spectra of these products are shown in Fig. 1. The amount of the product eluted at 60 min was negligibly small and the identification could not be done. The products eluted at 5, 15, and 22 min were the same as those obtained in the cases of *cis*- and *trans*-2-butenes. The yield of ethanamine, however, was negligibly small. The relative yields of the products are shown in Table 3. Similar to the cases of *cis*- and *trans*-2-butenes, the relative yields were almost constant for the changes in the experimental conditions.

Isobutene. In the case of isobutene, four products were separated at 20, 26, 33, and 41 min. The products eluted at 20 and 26 min were identified to be 2,2-dimethylaziridine and 2-methyl-2-propene-1-amine from their mass spectra, shown in Fig. 1, and their NMR spectra. The products eluted at 33 and 41 min were negligibly small and were not identified. The yields of the products relative to nitrogen are shown in Table 4. In contrast to the cases of 2- and 1-butenes, the relative yields of 2,2-dimethylaziridine decreased with the increases in the irradiation time and the concentration of hydrogen azide. The difference in the reaction cell, quartz or Pyrex, did

Table 3. The yields of the products relative to that of nitrogen obtained in the photolysis of hydrogen azide in the liquid 1-butene at 0 °C

$[HN_3]$ mmol dm^{-3}	IT[b)] min	NH_3	EA (38)	3B2A (15)	3B1A (26)	C (22)
83[c)]	30	—	0.17	0.10	0.13	0.01
85[c)]	60	0.29	0.19	0.12	0.16	0.02
85[c)]	90	0.33	0.15	0.15	0.17	0.01
83[d)]	30	0.22	0.23	0.08	0.15	0.03
154[c)]	30	0.26	0.22	0.12	0.15	0.03
154[c)]	60	0.26	0.21	0.15	0.17	0.02
Average		0.27 ±0.04	0.19 ±0.03	0.12 ±0.03	0.15 ±0.02	0.02 ±0.01

a) The abbreviations of the products are EA=2-ethylaziridine, 3B2A=3-butene-2-amine, and 3B1A=3-butene-1-amine. C was the same products obtained in the case of 2-butene, see Text. The values in the parentheses are the retention times of the products. b) IT=Irradiation time. c) A Pyrex cell was used. d) A quartz cell was used.

Table 4. The yields of the products relative to that of nitrogen obtained in the photolysis of hydrogen azide in the liquid isobutene[a)]

$[HN_3]$ mmol dm^{-3}	Cell[b)]	IT[c)] min	NH_3	DMA (20)	2MPA (26)
11[d)]	Q	20	0.15	0.42	0.26
16[e)]	Q	20	0.18	0.41	0.23
32[d)]	Q	20	0.19	0.42	0.25
33[e)]	Q	20	0.19	0.43	0.23
47[e)]	Q	20	0.20	0.37	0.23
63[e)]	Q	40	0.29	0.25	0.28
63[e)]	P	60	0.24	0.28	0.28
63[e)]	P	90	0.25	0.17	0.27
64[e)]	Q	20	0.22	0.38	0.24
64[e)]	Q	60	0.24	0.16	0.28
65[e)]	P	40	0.21	0.38	0.27
65[d)]	Q	20	0.20	0.37	0.25
77[e)]	Q	20	0.20	0.35	0.24
96[e)]	Q	20	0.20	0.38	0.25
118[d)]	Q	20	0.20	0.33	0.25
126[e)]	Q	20	0.21	0.31	0.26
148[e)]	Q	40	0.31	0.12	0.30
154[e)]	Q	20	0.23	0.28	0.26
155[e)]	P	30	0.22	0.14	0.26
157[e)]	P	60	0.22	0.07	0.25

a) The abbreviation of the products are DMA=2,2-dimethylaziridine and 2MPA=2-methyl-2-propene-1-amine. The values in the parentheses are the retention times of the products. b) Two kinds of the cell were used: Q=quartz and P=Pyrex. c) IT=Irradiation time. d) Reactions at the temperature of Dry Ice-methanol. e) Reactions at 0 °C.

not make a difference in this trend, although the effective wavelengths of the light in the former are slightly shorter than those in the latter. These results suggested that the aziridine formed was decomposed by the secondary process. The relative yields of 2,2-dimethylaziridine at the zero irradiation time was estimated to be about 0.45 by the extrapolation.

Discussion

Main Products. In the photolyses of hydrogen azide in the liquid C_4 olefins, the main products observed were nitrogen, ammonia, amines, and aziridines. The formation of these products is expected from the reaction mechanism proposed in the previous paper.[1)] The reaction mechanism proposed is shown as follows:

$$HN_3 + h\nu \longrightarrow {}^1NH + N_2 \qquad (1)$$

$$^1NH + Ol \longrightarrow \text{aziridine} \qquad (2)$$

$$\longrightarrow \text{amine} \qquad (3)$$

$$\longrightarrow {}^3NH + Ol \qquad (4)$$

$$^3NH + HN_3 \longrightarrow NH_2 + N_3 \qquad (5)$$

$$NH_2 + HN_3 \longrightarrow NH_3 + N_3 \qquad (6)$$

$$N_3 + Ol \longrightarrow OlN + N_2, \qquad (7)$$

where ^1NH and ^3NH represent the NH radicals in the excited singlet state, $NH(a^1\Delta)$, and in the ground triplet state, $NH(X^3\Sigma^-)$, respectively. Ol stands for olefin.

Reaction 2 is the addition reaction of the NH singlet to the double bond of olefin: *cis*- or *trans*-2,3-dimethylaziridine from *cis*- or *trans*-2-butene, 2-ethylaziridine from 1-butene, and 2,2-dimethylaziridine from isobutene. The addition occurs by a concerted manner ((a) process); in fact, only *cis*-aziridine was formed from *cis*-2-butene and only *trans*-aziridine from *trans*-2-butene.

Reaction 3 is the insertion reaction of the NH singlet into the C–H bond of olefin: *cis*- or *trans*-2-butene-1-amine from *cis*- or *trans*-2-butene, 3-butene-1- and 2-amines from 1-butene, and 2-methyl-2-propene-1-amine from isobutene. These products were all observed to be formed in good yield.

Role of Triplet NH Radicals. The triplet NH radical formed by a deactivation, Reaction 4, is assumed to abstract a hydrogen atom from hydrogen azide, Reaction 5. The triplet NH radicals possess enough energy to abstract an allylic hydrogen atom from olefin:

$$^3NH + Ol \longrightarrow NH_2 + R. \qquad (8)$$

Reaction 8, however, may be unimportant at the low temperature since the activation energy of Reaction 8 is expected to be high. If Reaction 8 is important and the resultant allyl radical abstracts a hydrogen atom from hydrogen azide,

$$R + HN_3 \longrightarrow Ol + N_3, \qquad (9)$$

Reaction 8 followed by Reaction 9 is indistinguishable from Reaction 5.[1)]

In the cases of the triplet methylene and oxygen, the addition to the double bond of the olefin has been considered to be important.[8,9)] The triplet NH radicals might add to the double bond of the olefin in this way:

$$^3NH + Ol \longrightarrow \text{triplet biradical.} \qquad (10)$$

If Reaction 10 competed with Reaction 5, the yield of ammonia would increase with an increase in the concentration of hydrogen azide. The yield observed, however, was almost constant for the changes in the concentration. If Reaction 10 competed with Reaction 8, the observed concentration dependence could be explained. In this case, we should expect the difference in the yield of ammonia between ethylene and propene or butenes, since the number of allylic C–H bonds included is different. The yield of ammonia also should increase with the reaction temperature. The yield of ammonia, however, was almost constant for the changes in the reactant and also in the reaction temperature. This inconsistency could be eliminated by assuming that ammonia is formed by a reaction in which the NH singlet abstracts two hydrogen atoms from an olefin:

$$^1\mathrm{NH} + \mathrm{Ol} \longrightarrow \mathrm{NH_3} + \text{products.} \qquad (11)$$

As was discussed in the previous paper, Reaction 11 is unlikely.[1)]

If Reaction 10 be included in the mechanism, the triplet biradicals will form aziridine by a ring closure, as observed in the cases of methylene or oxygen:[8,9)]

$$\text{triplet biradical} \longrightarrow \text{aziridine.} \qquad (12)$$

The aziridine formed by Reaction 12 should contain two geometrical isomers in the case of 2-butene: *cis*- and *trans*-2,3-dimethylaziridine. The results obtained, however, were different from this expectation. Thus we may conclude that the triplet NH radicals rarely add to the double bond of olefin under the present experimental conditions. This conclusion is different from that obtained in the cases of the triplet CH_2 and O. The low reactivity of the NH triplet has recently been suggested by the *ab initio* calculation. Fueno calculated the activation energy of the reaction of the NH triplet with ethylene to be 57 kJ mol^{-1}.[16)] For the reactions of the triplet O atoms with ethylene, the activation energy has been estimated to be about 6 kJ mol^{-1}.[17)]

Material Balance. From the above reaction mechanism, Reactions 1—7, the following relation can be expected to hold between the relative yields of products:

$$(\text{aziridine}+\text{amine}+3\mathrm{NH_3})/\mathrm{N_2} = 1.0. \qquad (13)$$

Using the values shown in Tables 1—4, the left-hand-side of Eq. 13 was estimated to be 1.2, 1.2, 1.3, and 1.4 respectively for *cis*- and *trans*-2-butenes, 1-butene, and isobutene. In the above estimations, the yields of minor products were neglected. Although the detailed mechanism for the minor product formations cannot be specified at present, these products may probably result from OlN, the product of Reaction 7. In the cases of ethylene and propene, the similar product ratios were found to be 0.7 and 0.96 respectively[1)] The small values were tentatively explained by neglecting the ethenamine formation. Ethenamine is a possible insertion product of the NH singlet into the vinylic C–H bond, but this compound is known to be unstable. In the cases of butenes, the sum of the relative yields, the left-hand-side of Eq. 13, were all larger than unity. This may be attributed to the large experimental errors, especially due to the indirect method of estimating the sensitivities of GLC and an incomplete reaction mechanism in which the formation of the minor products is neglected.

Relative Rate of the Insertion and the Addition. Using the values shown in Tables 1—4, the rate of the insertion into the allylic C–H bond can be estimated relative to that of the addition as follows: 0.7_1 (*cis*-2-butene), 0.6_7 (*trans*-2-butene), 0.5_2 (1-butene), and 0.5_7 (isobutene). The relative rate obtained with propene was 0.35.[1)] Except for the case of 1-butene, the relative rate per bond was almost equal and about 0.1. In other words, the rate of the insertion into an allylic C–H bond is about 1/10 that of the addition to the double bond of olefin. The large insertion rate obtained with 1-butene may be explained by the fact that the allylic C–H bond of 1-butene is weaker than others.

The authors are much obliged to Professor Takeshi Nakai of this Institute for the NMR analyses.

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