stable. However, the Pd^{II}-catalyzed oxidation of olefins, which has been established to proceed via such a metal complexation, reveals a structure–reactivity relationship quite different from the one observed here. Methyl substitutions, for instance, reduce the reactivity of alkenes.[28] Likewise, the stabilities of Ag^+–olefin complexes are reduced by the alkyl substitutions.[29,30] In addition, cis isomers usually form more stable Ag^+ complexes.[29,30]

Sharpless questioned why the electron-rich oxygen terminus of OsO_4 should attack an olefin electrophilically.[15] As noted above, the electrophilic nature of the osmium reaction is not very strong, and the charge-transfer interaction is important at the transition state. In other words, the reaction must be orbital-overlap controlled rather than net-charge controlled. The effect of net-charge density, if any, would be of secondary importance, and the reaction could well be electrophilic because of the presence of a low-lying vacant orbital (LUMO) in OsO_4.[31] The transition state like II is reasonable also from the orbital-symmetry considerations.[32]

Registry No. **1**, 107-25-5; **2**, 109-92-2; **3**, 926-65-8; **4**, 926-02-3; **5**, 111-34-2; **6**, 109-53-3; **7c**, 4696-25-7; **7t**, 4696-26-8; **8c**, 4188-64-1; **8t**, 4188-65-2; **9c**, 10034-12-5; **9t**, 10034-13-6; **10c**, 4884-01-9; **10t**, 1528-20-7; **11c**, 16969-28-1; **11t**, 16969-13-4; **12**, 927-61-7; **13**, 926-66-9; **14**, 100-42-5; **15**, 592-41-6; **16c**, 6443-92-1; **16t**, 14686-13-6; **17**, 96-33-3; **18t**, 623-43-8; **19**, 80-62-6; $KMnO_4$, 7722-64-7; OsO_4, 20816-12-0.

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Effects of Phenyl and Alkyl Substitutions on the Hydrogenation of Allene with Diimide

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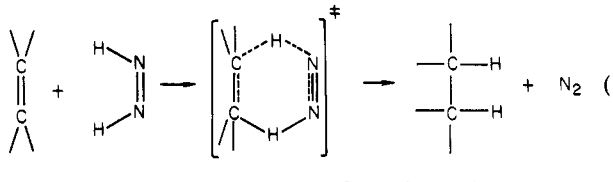
Hydrogenation of phenylpropadiene, 3-phenyl-1,2-butadiene, 1-phenyl-1,2-butadiene, and 1-phenyl-1,2-pentadiene with diimide (HN=NH) in refluxing methanol was conducted. The product distribution was analyzed as a function of reaction time, and the selectivities of the addition as well as relative reactivities were determined. Adverse steric effects of the phenyl group at the terminus of one double bond against "cis-coplanar" attack of diimide on the other double bond were found to be remarkably large. Alkyl groups activated the remote double bond of alkylallenes noticeably. This apparent electronic effect was theoretically rationalized from ab initio STO-3G model calculations of the chemical interactions.

Reactions of allenes have attracted the interest of organic chemists because of their variety in possible modes of reaction. Results of extensive work on the selectivity in addition reactions of allenes are summarized in reviews.[1-3] However, the cause of the selectivity is not well understood yet. Electronic effects of substituents were previously analyzed on the basis of NMR observations.[4] Quantitative treatments of the chemical reactivities are limited.[5,6] More precisely, a decomposition of the reactivity by each reaction mode has never been undertaken because of practical difficulties. Stepwise reactions of allenes involving allylic intermediates result in the formation of thermodynamically stable products, irrespective of kinetic selectivities; product distribution does not necessarily reflect kinetic selectivity.[7]

Contrastingly, one-step reactions give rise to the kinetically governed product distributions. For such a reaction, hydrogenation of double bonds by diimide is simple and well characterized as described in reviews.[8,9] The reaction proceeds in a concerted manner through a six-membered cyclic transition state to give a syn adduct[10] (eq 1).


(1)

In the present paper, the diimide hydrogenation of phenylpropadiene (**1a**) and its derivatives (**1b–d**) has been investigated to analyze the selectivity. Attention was focused upon the characteristic effects dependent on the structure of allene due to the mutually orthogonal cumulated double bonds. That is, how would the electronic effect of an α-substituent X be transmitted through the

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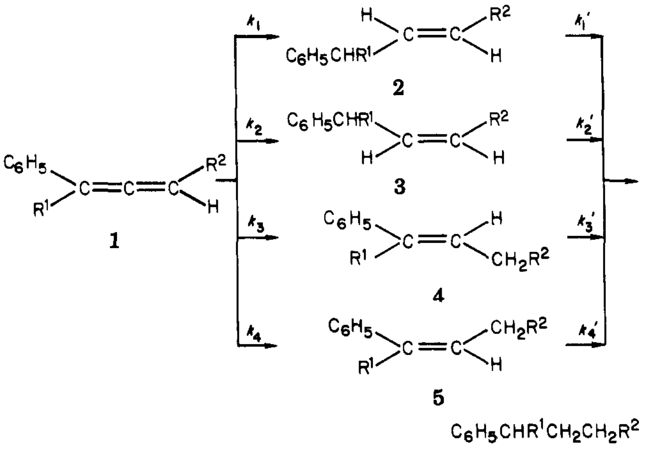
0022-3263/80/1945-1604$01.00/0

Table I. Relative Rate Constants Obtained by Curve Fitting

allene	k_1/k	k_2/k	k_3/k	k_4/k	k_1'/k	k_2'/k	k_3'/k	k_4'/k
1a	0.09	0.09	0.03	0.79	1.80	1.80	0.55	0.30
1b	0.045	0.045	0.16	0.75	0.025	0.025	0.21	0.11
1c	0.28	0.48	0.03	0.21	0.57	0.50	0.68	0.50
1d	0.16	~0.56	(0.005)	~0.28	0.98	0.77	0.88	0.60

Scheme I[a]



[a] a, $R^1 = R^2 = H$; b, $R^1 = CH_3$, $R^2 = H$; c, $R^1 = H$, $R^2 = CH_3$; d, $R^1 = H$, $R^2 = C_2H_5$.

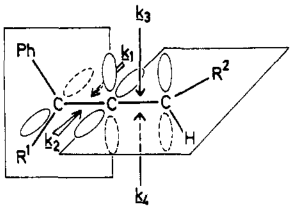
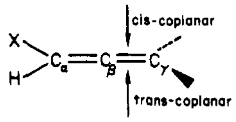


Figure 1. Modes of the diimide attack on phenylallenes.

orthogonal double bonds? Further, how large should the steric effect of the substituent against the "cis-coplanar" approach of the reagent be as compared with the "transcoplanar" approach?



It was found that the phenyl group sterically inhibits the cis-coplanar approach of diimide to phenylallenes while the alkyl group electronically activates the remote double bond of alkylallenes.

Results

The hydrogenation of the allene under study is expected to proceed stepwise according to Scheme I. Hydrogenation at the α,β bond will give rise to intermediates **2** and **3** with the respective rate constants k_1 and k_2, while the reaction at the β,γ bond will provide **4** and **5**, the rate constants being k_3 and k_4. A stereochemical view of the four attacking modes (k_1–k_4) is illustrated in Figure 1. The two reaction modes at the α,β bond (k_1 and k_2) are identical if $R^2 = H$ (**1a, b**). The alkenylbenzenes (**2–5**) are subject to further hydrogenation to give eventually the saturated product **6**. We will denote the rate constants of this second step of hydrogenation by k_1'–k_4'.

All the expected products **2–6** were identified by comparing their gas chromatographic retention times with

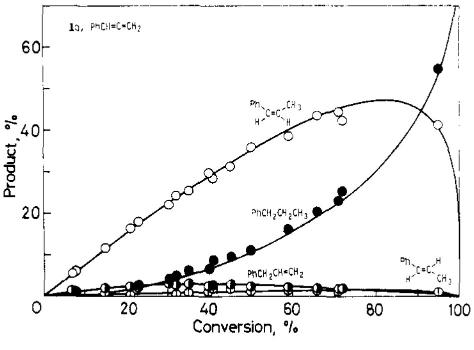


Figure 2. Product distributions against the extent of reaction of **1a**: ◑, **2a**; Φ, **4a**; ○, **5a**; ●, **6a**.

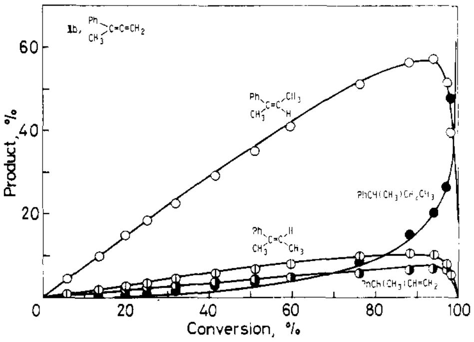


Figure 3. Product distributions against the extent of reaction of **1b**: ◑, **2b**; Φ, **4b**; ○, **5b**; ●, **6b**.

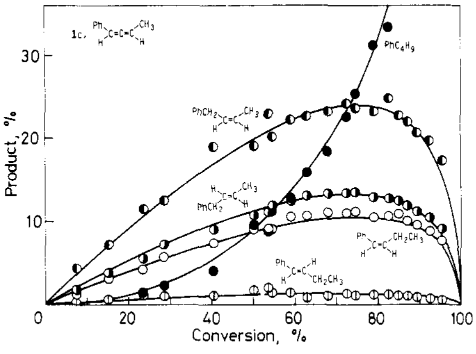


Figure 4. Product distributions against the extent of reaction of **1c**: ◑, **2c**; ◐, **3c**; Φ, **4c**; ○, **5c**; ●, **6c**.

those of the authentic samples. Although the authentic sample of **2b** was not available, five of the six well-separated peaks observed on the gas chromatogram of the reaction mixture of **1b** corresponded to **1b**, **4b**, **5b**, **6b**, and anisole (the internal standard used); the remaining peak was thus assigned to **2b**. In no case were there other unexpected products discernible. Furthermore, material balances for the reactants and products were at all times perfect to within the experimental error of ±5%.

The distributions of the product alkenylbenzenes (**2–5**) and alkylbenzene (**6**) are plotted against the extent of reaction of the allene **1** in Figures 2–5. In each case, the expected alkenylbenzenes were formed at the initial step and then suffered further hydrogenation to give the alkylbenzene final product. The curves drawn are theoretical ones calculated by using the equations given in the Ex-

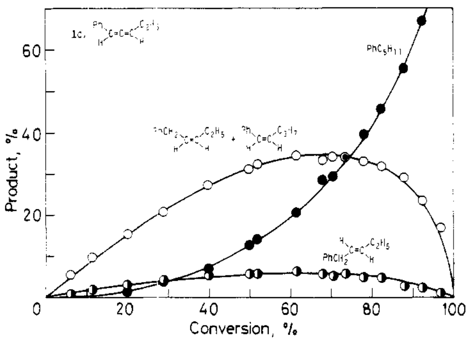


Figure 5. Product distributions against the extent of reaction of **1d**: ◑, **2d**; ○, **3d** and **5d**; ●, **6d**.

Table II. Relative Reactivities of Allenes

allene	$\bar{k}$	$\bar{k}_1$	$\bar{k}_2$	$\bar{k}_3$	$\bar{k}_4$
1a	100	9.0	9.0	3.0	79
1b	33.9	1.5	1.5	5.4	25.4
1c	74.6	20.9	35.8	2.2	15.7
1d	50.4	8.1	~28	(0.3)	~14

perimental Section. The rate parameters used are given in Table I.

In the analysis of the reaction of **1d**, chromatographic separation of **3d** and **5d** was poor, **5d** appearing as a shoulder on the peak of **3d**. The peak areas of **3d** and **5d** and hence their concentrations were obtained as sums, from which the rate parameter, $k_2/k + k_4/k$, of 0.84 was evaluated. The product ratio **3d**/**5d** was determined for some samples of low conversion (<10%) by comparing the shape of peaks with those of controlled mixtures of the authentic samples. The best product ratio thus obtained was 2/1, which led to the relative rates $k_2/k = 0.56$ and $k_4/k = 0.28$ for **1d**. The peak of **4d** was negligibly small, the maximum fraction being about 0.2% at 50% conversion. The situation was reproduced by adopting the value $k_3/k = 0.005$.

The relative reactivities of alkenylbenzenes **2**–**5** of the various substitution types (**a**, **b**, **c**, and **d**) were determined separately by competitive experiments.[11] It was verified that, for *each* substitution type, the results of the competitive experiments were indeed in good accord with the k_i'/k values given in Table I. From the competitive reactivity values for relevant alkenylbenzenes,[11] we can evaluate the overall relative reactivities k of the allenes of *different* substitution types (**1a**–**d**). Such k values in turn permit calculation of all the k_i and k_i' values relative to a single common reference. The k_i values thus obtained are listed in Table II, where the k value of **1a** was chosen to be 100 for the sake of easier comparison. The relative rate constants on the present conventional basis are expressed as $\bar{k}$ and $\bar{k}_i$. One may likewise define $\bar{k}_i'$ values on the same basis, but in what follows discussion will be confined to the $\bar{k}_i$ values for phenylallenes.

Discussion

Effects of Substituents. Inspection of data given in Table II indicates that the overall reactivity of **1a** is reduced by alkyl substitution although the effect is small as compared with that on the reactivity of styrene.[11] Interpretation of these results is complex because of the variety of possible reaction modes of the allenes. However, comparisons of the individual rates of the diimide attack ($\bar{k}_1$–$\bar{k}_4$) provide a good deal of interesting information.

Hydrogenation of **1a** takes place mainly (79%) at the terminal bond from the side distant from the phenyl group (trans-coplanar attack, $\bar{k}_4$). The attack on the same bond from the side of the phenyl group (cis-coplanar attack, $\bar{k}_3$) occurs least readily (3.0%). The relative ease of these two modes of attack ($\bar{k}_3/\bar{k}_4 = 3.0/79 = 0.038$) must be due to the steric bulk of the phenyl group relative to a hydrogen atom. Similar comparisons of the effects of phenyl and methyl groups are possible with **1b**. The $\bar{k}_3/\bar{k}_4$ ratio $5.4/25.4 = 0.21$ of **1b** is due to the relative steric bulk of the phenyl in comparison to the methyl group. Apparently, the increase in the ratio is due to the greater steric bulk of the methyl group compared to a hydrogen atom; the difference ($0.038/0.21 = 0.18$) is due to the steric effects of the α-methyl group. These results indicate that the substitution of an α-hydrogen by a more bulky group exerts serious adverse steric effects against the cis-coplanar attack at the β,γ bond.

If the effects of substituent on the remote bond were solely due to the steric cause, the $\bar{k}_3$ values for **1a** and **1b** should be equal to each other. In reality, the $\bar{k}_3$ value of **1b** was found to be 1.8 times greater than that of **1a**. Therefore, electronic effects of the α-methyl group must be operating on the β,γ bond.

An even more dramatic rate-enhancing effect of the methyl group was perceived in the hydrogenation of **1c**. That is, both $\bar{k}_1$ (20.9) and $\bar{k}_2$ (35.8) values of **1c** are greater than the corresponding value (9.0) of **1a**. Comparison of the $\bar{k}_2$ values, which would suffer little steric effect, shows that the γ-methyl group enhances the rate of hydrogenation of the α,β bond of **1a** by a factor of 4.0. The γ-ethyl group of **1d** exhibits a similar rate-enhancing effect by a factor of 3.1. These findings are rather surprising in view of the customary belief that the diimide hydrogenation is almost insensitive to electronic effects; no indication of rate-enhancing effects has hitherto been noted with alkyl substituents in alkenes.[8-12] In addition, the smaller $\bar{k}_1$ values as compared to the $\bar{k}_2$ values for both **1c** and **1d** could be ascribed to the steric effects of the methyl and ethyl groups, respectively. The effects are relatively small; $\bar{k}_1/\bar{k}_2 = 0.58$ (**1c**) and 0.29 (**1d**).

The effects of substituents directly attached to the carbon atom of a reacting double bond are much the same as those already found with alkenes. The steric-bulk effect of the phenyl group may be estimated by the comparison of $\bar{k}_1$ (or $\bar{k}_2$) with $\bar{k}_4$ for **1a**, the ratio being $9.0/79 = 0.11$. Similarly, the effects of the methyl group can be evaluated by comparing the $\bar{k}_1$ (or $\bar{k}_2$) values for **1b** and **1a** ($1.5/9.0 = 0.17$) or by comparing the $\bar{k}_4$ values for **1c** and **1a** ($15.7/79 = 0.20$). The adverse effects of direct substitutions on the magnitudes of 0.1 and 0.2 for the phenyl and methyl groups, respectively, are in accord with the results with alkenes.[8-12]

Theoretical Considerations. In order to gain a better understanding of the effects of alkyl substitution, we carried out an interaction-energy decomposition analysis for the allene–diimide systems. The interaction energy ΔE between two reactants is expressed as a sum of the electrostatic (ES), polarization (PL), exchange-repulsion (EX), and charge-transfer terms (CT)[13] (eq 2).

$$\Delta E = \mathrm{ES} + \mathrm{PL} + \mathrm{EX} + \mathrm{CT} \qquad (2)$$

We calculated ΔE for ethylene, propadiene, and 1,2-butadiene as model compounds. The ab initio (STO-3G)

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[11] Toyoshima, K. Doctoral thesis submitted to Osaka University, 1979. Competitive rates for a set of **5a,b,c,d**, for instance, were 18, 2.2, 22, and 18, respectively, relative to **2b**.

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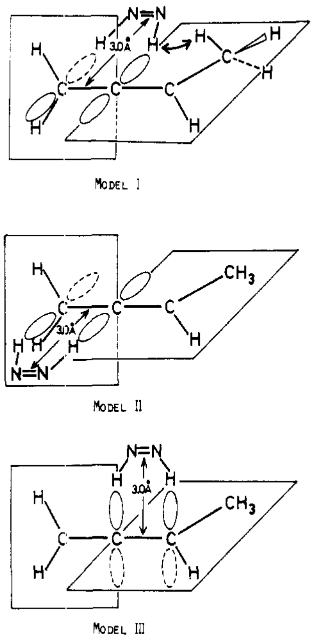

Figure 6. Model geometries assumed for the interaction of diimide with 1,2-butadiene.

Table III. Energy Component Analysis for the Hydrogenation of Ethylene, Propadiene, and 1,2-Butadiene with Diimide[a]

	ethylene	propadiene	1,2-butadiene II[b]	1,2-butadiene III[b]
ES	-3.3	-3.8	-4.1	-4.1
EX	10.3	13.5	13.6	14.7
PL	-0.1	-0.2	-0.2	-0.2
CT	-5.4	-4.3	-4.7	-4.0
ΔE	1.5	5.2	4.7	6.4

[a] Energies are given in units of kcal/mol. [b] Models II and III.

method was used. For the reaction of 1,2-butadiene, three different approach models (I–III, as illustrated in Figure 6) were considered. In all cases, *cis*-diimide was placed above the reacting C–C double bond in such a manner that the diimide and the carbon π orbitals were coplanar and had a local C_{2v} symmetry. Similar models were adopted for ethylene and propadiene. The distance between the reacting double bond and the N=N bond of *cis*-diimide was fixed at 3.0 Å.[14] For the sake of convenience, all the reactant molecules were assumed to persist in their respective standard geometries. The results of the calculation are given in Table III.

Comparing the interaction energies for ethylene with those for propadiene, we find that the differences in attractive energy terms are all relatively small. This is probably because the electronic character of the double bond of propadiene is not much different from that of ethylene. The greater repulsive interaction energy ΔE for propadiene is largely due to the EX energy, indicating the significance of the repulsion between the intact methylene group of propadiene and a diimide hydrogen.

As for 1,2-butadiene, model I (approach is cis-coplanar to the methyl group) was found to be extremely unfavorable (calculation results not listed). This is because of an extraordinarily large EX term arising as a result of too small an assumed distance (0.88 Å) between the hydrogen atoms of the methyl group and diimide.

With model III, the ES stabilization energy (-4.1 kcal/mol) is greater in magnitude than that found for propadiene (-3.8 kcal/mol) while the CT energy of the former (-4.0 kcal/mol) is smaller in magnitude than that obtained for the latter (-4.3 kcal/mol). The results, when combined, indicate that the substitution of methyl for an allene hydrogen hardly exerts any electronic influence on the double bond carrying the methyl group. The greater reaction barrier ΔE of model III (6.4 kcal/mol) than that found for propadiene (5.2 kcal/mol) is due mainly to the larger EX energy. The situations were found to be similar with ethylene and propene. The results suggest that the adverse steric effect of the methyl substituent is indeed a crucial factor which affects the reactivity of the double bond bearing an alkyl substituent.

The reaction barrier for model II (approach is trans-coplanar to the methyl group) is 0.5 kcal/mol smaller than that for propadiene. Apparently, this is due to the greater attractive interactions, i.e., ES and CT. The close agreement between the EX energies for propadiene (13.5 kcal/mol) and model II (13.6 kcal/mol) suggests that the activation of the C_1–C_2 double bond of 1,2-butadiene must be due to the electronic effect. These results rationalize the view that an alkyl group activates the remote double bond of allene electronically.

In conclusion, the adverse steric effects of the phenyl group are very large against the cis-coplanar attack on the remote double bond of allene. On the other hand, an alkyl group can electronically activate the remote double bond while it tends to sterically deactivate the double bond to which it is directly attached.

Experimental Section

Materials. Phenylpropadiene (**1a**), 3-phenyl-1,2-butadiene (**1b**), and 1-phenyl-1,2-butadiene (**1c**) were obtained as described previously.[5] 1-Phenyl-1,2-pentadiene (**1d**) was prepared from 1-phenyl-1-butene in the same way: bp 95–97 °C (20 mmHg); IR (thin film) 1944, 890 cm^{-1}; NMR (CCl_4) δ 1.08 (3 H, t, CH_3), 2.18 (2 H, m, CH_2), 5.68 (1 H, q, =CHEt), 6.20 (1 H, m, PhCH=).

3-Phenyl-1-propene (**2a**) was prepared by the Grignard method from bromobenzene and allyl bromide; bp 64–65 °C (30 mmHg) [lit.[16] bp 154 °C (725 mmHg)]. (*E*)-1-Phenyl-2-butene (**2c**) was purchased from Tokyo Kasei Co. and distilled. (*E*)-1-Phenyl-2-pentene (**2d**) containing a small amount of *Z* isomer was prepared from 3-hydroxy-1-phenyl-1-pentene[17] which was obtained by the reaction of ethylmagnesium bromide and cinnamaldehyde;[18] bp 63–64 °C (3 mmHg) [lit.[19] bp 80° C (12 mmHg)]. The *Z* isomers (**3c,d**) of **2c,d** were obtained only as mixtures of isomers by photochemical isomerization of the respective *E* isomers (**2c,d**):[20] bp 80–85 °C (30 mmHg for a 1:9 mixture of **2c** and **3c**); bp 60–62 °C (2 mmHg for a 4:6 mixture of **2d** and **3d**).

2-Phenyl-2-butenes **4b** and **5b** were prepared by the method of Cram.[21] **4b**: bp 90–92 °C (25 mmHg); n^{25}_{D} 1.543 (lit.[21] bp 193 °C; n^{25}_{D} 1.5402). Isomeric mixture (6/4 **4b**/**5b**): bp 90–91 °C (22 mmHg); n^{25}_{D} 1.533 (for **5b**, lit.[21] bp 173 °C; n^{25}_{D} 1.5193).

1-Phenyl-1-alkenes rich in *E* isomers (**4a,c,d**) were prepared by dehydration of the corresponding alcohols.[22] Samples rich in *Z* isomers (**5a,c,d**) were obtained by careful distillations.

Alkylbenzenes **6**, anisole, tetraline, *n*-pentane, and *p*-toluenesulfonylhydrazine were commercially obtained. Triethylamine

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(14) The geometry of the transition state for the reaction of ethylene and diimide has recently been fully optimized,[15] and the distance between two reactants was about 2.5 Å.

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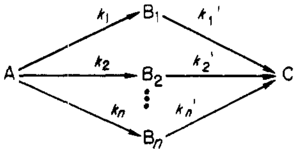
was distilled from NaOH. Methanol was purified by distillation from Mg activated with I_2.

Procedure. A reaction mixture consisting of allene (0.3 g), *p*-toluenesulfonylhydrazine (1.0 g), triethylamine (0.75 mL), an internal standard (0.1 g), and methanol (2 mL) was heated under reflux in a small flask equipped with a reflux condenser. At appropriate time intervals, the reaction mixture (0.05 mL) was withdrawn from the top of the condenser by use of a syringe with a long needle (20 cm), poured into a sample tube, and quenched by the addition of water (2 mL) and *n*-pentane (0.1 mL). The mixture was shaken vigorously, and the upper organic layer was subjected to VPC analysis. A gas chromatograph (Shimadzu 4APT) with a 4-m column of silicone XF-1150 was used. Only the expected peaks of the products were found along with those of the reactant allene and the internal standard. The peaks were assigned by comparing the retention times with those of authentic samples. The concentrations of reactants and products were determined by the internal standard method on the basis of the peak areas which were evaluated by integration on a Hitachi HITAC-10 computer. The internal standards used were cumene, anisole, *sec*-butylbenzene, and tetraline for the reactions of **1a–d**, respectively.

Kinetic Analysis. The distribution of various products was analyzed according to the reactions shown in Scheme I. The problem is essentially that of the consecutive, competitive first-order reactions as follows:



Integration of the relevant rate equations readily gives the molar fractions of A, B_1–B_n, and C at time *t* (eq 3a–c), where $[A]_0$ is the initial concentration of *A*, $i = 1, 2, ..., n$, and *k* is an overall first-order rate constant (eq 4).

$$\alpha \equiv [A]/[A]_0 = e^{-kt} \quad (3a)$$

$$\beta_i \equiv [B_i]/[A]_0 = \frac{k_i}{k_i' - k}(e^{-kt} - e^{-k_i't}) \quad (3b)$$

$$\gamma \equiv [C]/[A]_0 = 1 - \alpha - \sum_i \beta_i \quad (3c)$$

$$k = \sum_i k_i \quad (4)$$

For our present purpose, we express β_i as the function of the extent of reaction x (=1 − α) of A. The result is given in eq 5.

$$\beta_i = \frac{(k_i/k)}{(k_i'/k) - 1}[1 - x - (1 - x)^{k_i'/k}] \quad (5)$$

β_i attains a maximum when x reaches η_i such that

$$\eta_i = 1 - (k_i'/k)^{-1/[(k_i'/k) - 1]} \quad (6)$$

The value of β_i at the maximum is given in eq 7. Equations 6

$$\beta_{i,\max} = (1 - \eta_i)(k_i/k)/(k_i'/k) \quad (7)$$

and 7 greatly assist us in evaluating k_i/k and k_i'/k from the experimental curves. The curve fittings were accomplished by use of a Yokokawa-Hewlett-Packard Model 20 computer.

MO Computation. All calculations were performed within the framework of the ab initio restricted Hartree–Fock theory by employing a modified version of the GAUSSIAN 70 package.[23] The minimal STO-3G set was used with the suggested standard parameters.[24] As for the molecular geometries, standard bond lengths and angles proposed by Pople et al.[25] were employed.

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Registry No. 1a, 2327-99-3; **1b**, 22433-39-2; **1c**, 2327-98-2; **1d**, 2327-97-1; **2a**, 300-57-2; **2b**, 934-10-1; **2c**, 935-00-2; **2d**, 51795-73-4; **3c**, 15324-90-0; **3d**, 37549-95-4; **4a**, 873-66-5; **4b**, 768-00-3; **4c**, 1005-64-7; **4d**, 16002-93-0; **5a**, 766-90-5; **5b**, 767-99-7; **5c**, 1560-09-4; **5d**, 7642-18-4; **6a**, 103-65-1; **6b**, 135-98-8; **6c**, 104-51-8; **6d**, 538-68-1; ethylene, 74-85-1; propadiene, 463-49-0; 1,2-butadiene, 590-19-2; diimide, 3618-05-1.

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Geometries and Relative Energies of Some $C_6H_5^+$ and $C_5H_5Si^+$ Isomers. Pyramidal (Nido) vs. Planar, Cyclic Structures

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Ab initio molecular orbital calculations with geometry optimization at the STO-3G level have been carried out on pyramidal (**1**, **5**) and cyclic (**2**, **3**) $C_6H_5^+$ and $C_5H_5Si^+$ structures. Additional single-point calculations at the 4-31G ($C_6H_5^+$), 3-21G, and STO-3G* ($C_5H_5Si^+$) levels were performed to probe the effects of larger basis sets. Pyramidal structure **1**, with C_{5v} symmetry, places a carbon or a silicon atom in a position with a formal coordination number of five. Among the $C_6H_5^+$ isomers, the planar cyclic structures **2-C** and **3-C** are highly preferred over the pyramidal ones **1-C** and **5**, but there is a strong dependence of energies on the basis set employed. In contrast, the C_{5v} pyramidal $C_5H_5Si^+$ structure **1-Si** is favored over the planar, cyclic structures **2-Si** and **3-Si**. Whereas the phenyl cation **2-C** should have a singlet ground state, the silaphenyl cation **2-Si** is indicated to possess a triplet ground state. Analysis of the charge distributions illustrates the differences in electronic demands and bonding between C^+ and Si^+ species.

Recently, Aylett and Colquhoun[2] observed the fragment ion $C_5H_5Si^+$ with high relative intensities in the mass spectra of $SiH_2[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ and $SiCl_2[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$. The analogous ions $C_5H_5Ge^+$ and $C_5H_5Sn^+$

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