Aromatic Nucleophilic Substitution. 20.[1] Kinetics of the Reactions of 2-(Acetylamino)ethyl 2,6-Dinitrophenyl Ether and *N*-Acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline with Potassium Methoxide in Me_2SO–Methanol

Shizen Sekiguchi,* Motohiko Hirai, and Noboru Tomoto†

Department of Synthetic Chemistry, Gunma University, Kiryu, Gunma 376, Japan, and, Department of Industrial Chemistry, Miyazaki University, 1-1-1 Kirishima, Miyazaki, Miyazaki 880, Japan

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The reactions of 2-(acetylamino)ethyl 2,6-dinitrophenyl ether (**1e**) and *N*-acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (**6e**) with potassium methoxide were carried out in Me_2SO–methanol (60:40, *v*/*v*). In both reactions the same spiro anionic σ complex **3e** was formed, although the two rates of formation of **3e** were different. On the other hand, the rates of decomposition of **3e** were the same in both reactions within experimental error, both indicating that considerable amounts of **1e** and **6e** are initially converted into **3e**, which then undergoes unimolecular decomposition.

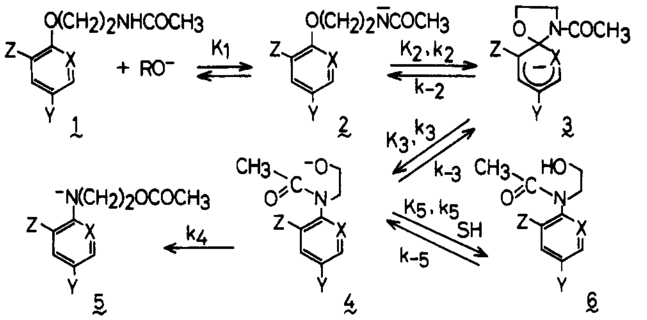
Although the Meisenheimer complexes in aromatic nucleophilic substitution reactions have attracted much attention,[2-4] there have been a few reports describing detailed kinetics of the base-catalyzed Smiles rearrangements (aromatic intramolecular nucleophilic substitution) where such complexes intervene.[5,6]

We have reported previously that in the Smiles rearrangement of **1a–d** (Scheme I) the process **1** ⇄ **2** ⇄ **3** is very fast whereas the process **3** ⇄ **4** → **5** is relatively slow.[7-10]

From the kinetics of the Smiles rearrangement of **1a–d**, the pseudo-first-order rate constant for the rearrangement (k_{obsd}) could be expressed as a function of K_2, K_3, and K_4, of which K_2 could be determined by a stopped-flow method. Accordingly, more detailed information of K_3, K_4, and K_5 is necessary for further characterization of the reaction. Although the kinetics of the reaction of **6a–d** with a base would contribute to the elucidation of those stages, we were not able to synthesize **6a–d**. More recently *N*-acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (**6e**) has been synthesized.[11,12]

The UV–vis and NMR time-dependent spectra of the potassium *tert*-butoxide catalyzed rearrangements of **1e** and **6e** indicated the reaction path shown in Scheme I.[11] This paper reports the kinetics of the reactions of **1e** and **6e** with CH_3OK in a Me_2SO–CH_3OH mixture (60:40, *v*/*v*).

Scheme I



	X	Y	Z	
a	CNO_2	NO_2	H	SH: solvent
b	CBr	NO_2	H	
c	CCN	NO_2	H	
d	N	NO_2	H	
e	CNO_2	H	NO_2	

Results

Stage I. Rearrangement of 2-(Acetylamino)ethyl 2,6-Dinitrophenyl Ether (1e). As the spectral evidence shows,[11] the reaction of **1e** or **6e** is divided into two stages. With **1e**,[11] the process **1e** ⇄ **2e** ⇄ **3e** (stage I) is very fast, whereas the process **3e** ⇄ **4e** → **5e** (stage II) is relatively slow. With **6e** the process **6e** ⇄ **4e** ⇄ **3e** (stage I) is very fast, whereas the process **3e** ⇄ **4e** → **5** (stage II) is relatively slow. Thus the stage I equilibrium is established rapidly, lying considerably to the right with higher [CH_3OK], and the decomposition of **3e** is relatively slow.[11]

Let us rewrite Scheme I as Scheme II in a fashion convenient for quantitative discussion of **1e**. The constant K_1 can be expressed as K_AK_1' (where K_A is the dissociation constants of **1e**, and K_1' is the self-association constant of methanol). In the kinetic measurement of the stage I reaction (eq 1 and 2), the stage II reaction can be neglected.

Scheme II

$$\mathbf{1e} + CH_3O^- \xrightleftharpoons{K_1} \mathbf{2e} + CH_3OH \tag{1}$$

$$\mathbf{2e} \xrightleftharpoons{k_3,\ K_3} \mathbf{3e} \tag{2}$$

$$\mathbf{3e} \xrightleftharpoons[k_{-3}]{k_3,\ K_3} \mathbf{4e} \xrightarrow{k_4} \mathbf{5e} \tag{3}$$

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(9) Okada, K.; Sekiguchi, S. *J. Org. Chem.* **1978**, *43*, 441. For the OH^--catalyzed rearrangement of **1b** at 25 °C, k_2 is 1.18×10^2 s^{-1}, k_{-2} is 1.10×10 s^{-1}, and K_1 is 1.31×10^2 M^{-1}; for the OH^--catalyzed rearrangement of **1d**, k_2 is 5.99×10^2 s^{-1}, k_{-2} is 1.20×10 s^{-1}, and K_1 is 9.33×10 M^{-1}.

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(12) Sekiguchi, S.; Hirai, M.; Tomoto, N. *Bull. Chem. Soc. Jpn.*, in press. The relationship between k_ψ^N and [$(CH_3)_2CHONa$] was found to be curvilinear in the reaction of **6e** with $(CH_3)_2CHONa$ in the Me_2SO–2-propanol (20:80) at 15 °C, from whose kinetics k_2K_1 is 326, k_{-2} too small to be determined, k_3 is 7.86 s^{-1}, k_{-3} is 1.82×10^4 s^{-1}, K_5^{-1} is 3.1 M^{-1}, K_3^{-1} is 2.3×10^3, and $K_3^{-1}K_5^{-1}$ is 7.1×10^{-3} M^{-1}, respectively.

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Table I. Temperature Dependence of Rate and Equilibrium Constants for the Formation of Spiro Anionic σ Complex 3e from 2-(Acetylamino)ethyl 2,6-Dinitrophenyl Ether (1e) or *N*-Acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (6e) and Potassium Methoxide in Me_2SO-CH_3OH (60:40, *v/v*)

temp, °C	k_2K_1, $M^{-1}\ s^{-1}$	k_{-2}, s^{-1}	K_1K_2, M^{-1}	$k_{-3}K_5^{-1}$, $M^{-1}\ s^{-1}$	k_3, s^{-1}	$(K_5K_3)^{-1}$, M^{-1}
15	*a*	*a*	*a*	418 ± 14	2.58 ± 0.25	164 ± 21
20	8.53 ± 0.31	*b*	*a*	655 ± 51	3.97 ± 0.94	178 ± 56
30	26.6 ± 0.7	*b* (0.118 ± 0.0021)[d]	232 ± 36[c]	1480 ± 120	7.45 ± 2.09	221 ± 78 (339 ± 89)[c]
40	62.7 ± 3.5	0.17 ± 0.11 (0.239 ± 0.036)[d]	246 ± 45[c]	4060 ± 260	10.7 ± 2.8	415 ± 133
50	140 ± 6	0.14 ± 0.09	*a*	*a*	*a*	*a*

[a] Not measured. [b] Too small to be evaluated from the kinetics. [c] Determined by a spectrophotometric method (see Experimental Section). [d] Calculated from $k_{-2} = (k_2K_1)/K_1K_2$.

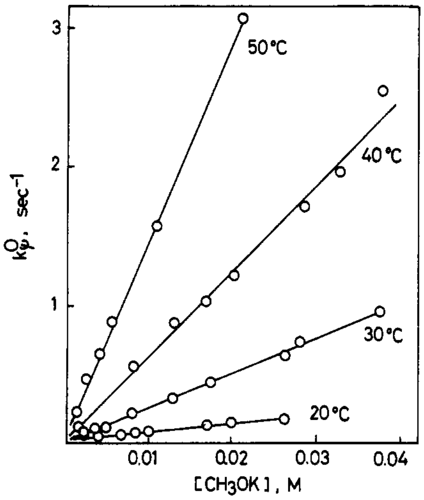

Figure 1. Relationship between k_ψ^O and $[CH_3OK]$ in the reaction of 2-(acetylamino)ethyl 2,6-dinitrophenyl ether (1e) with CH_3OK in Me_2SO-CH_3OH (60:40, *v/v*): $[1e]_0 = 3.67 \times 10^{-5}$ M; $\mu = 0.05$ M ($KClO_4$).

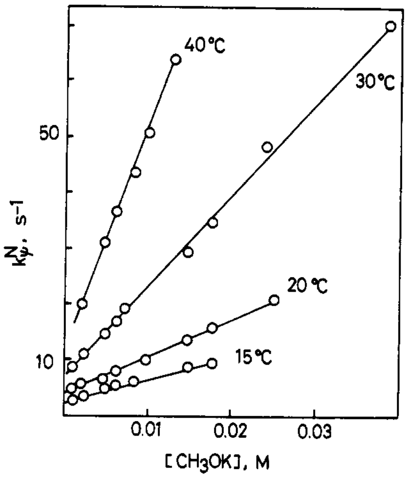

Figure 2. Relationship between k_ψ^N and $[CH_3OK]$ in the reaction of *N*-acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (6e) with CH_3OK in Me_2SO-CH_3OH (60:40, *v/v*): $[6e]_0 = 3.71 \times 10^{-5}$ M; $\mu = 0.05$ M ($KClO_4$).

Accordingly, the pseudo-first-order rate constant (k_ψ^O) for formation of 3e is expressed in eq 4.

$$k_\psi^O = k_{-2} + \frac{k_2K_1[CH_3OK]}{1 + K_1[CH_3OK]} \qquad (4)$$

If $K_1[CH_3OK] \ll 1$, eq 5 is derived. The dependence of k_ψ^O on $[CH_3OK]$ is compatible with eq 5 (Figure 1). As

$$k_\psi^O = k_{-2} + k_2K_1[CH_3OK] \qquad (5)$$

a result, the k_{-2} and k_2K_1 values can be estimated from the intercept and slope in the linear plots, respectively (Table I).

Rearrangement of *N*-Acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (6e). In the reaction of 6e with CH_3OK one can rewrite Scheme I as Scheme III. The constant

Scheme III

$$6e + CH_3O^- \underset{k_5,\ K_5}{\overset{k_{-5}}{\rightleftarrows}} 4e + CH_3OH \qquad (6)$$

$$4e \underset{k_3,\ K_3}{\overset{k_{-3}}{\rightleftarrows}} 3e \qquad (7)$$

$$3e \underset{k_{-3}}{\overset{k_3,\ K_3}{\rightleftarrows}} 4e \xrightarrow{k_4} 5e \qquad (8)$$

K_5 can be expressed as K_W/K_A (where K_A is the constant of 6e and K_W is the ionic product of methanol). In the kinetic measurement of the stage I reaction (eq 6 and 7) the stage II reaction can be neglected. The pseudo-first-order rate constant (k_ψ^N) for formation of 3e, is therefore expressed in eq 9 (note the relationships between the directions of reactions and rate or equilibrium constants).

$$k_\psi^N = k_3 + \frac{\dfrac{k_{-3}}{K_5}[CH_3OK]}{1 + \dfrac{1}{K_5}[CH_3OK]} \qquad (9)$$

Accordingly the plot of k_ψ^N against $[CH_3OK]$ should show a curvilinear dependence on $[CH_3OK]$, indicating a fixed value at higher $[CH_3OK]$. If $[CH_3OK]/K_5 \ll 1$, however, a linear dependence should be obtained (eq 10).

$$k_\psi^N = k_3 + \frac{k_{-3}}{K_5}[CH_3OK] \qquad (10)$$

Figure 2 shows the linear dependence of k_ψ^N on $[CH_3OK]$, giving the k_3 and k_{-3}/K_5 values from the intercept and slope in the linear plots.

In Table I, the K_1K_2 values were obtained by a spectrophotometric method, since the errors in k_{-2} values obtained by kinetic measurement were so large that exact K_1K_2 values were not obtained (refer to the k_{-2} values at 40 and 50 °C). The large K_1K_2 and $(K_5K_3)^{-1}$ values show that the equilibria for $1e + CH_3O^- \rightleftarrows 3e + CH_3OH$ and $6e + CH_3O^- \rightleftarrows 3e + CH_3OH$ lie considerably to the right at higher $[CH_3OK]$.

Stage II. Rearrangement of 2-(Acetylamino)ethyl 2,6-Dinitrophenyl Ether (1e). As the spectral results[11] and the stage I kinetics show, in the treatment of the kinetics of the stage II reaction the stage I reaction can

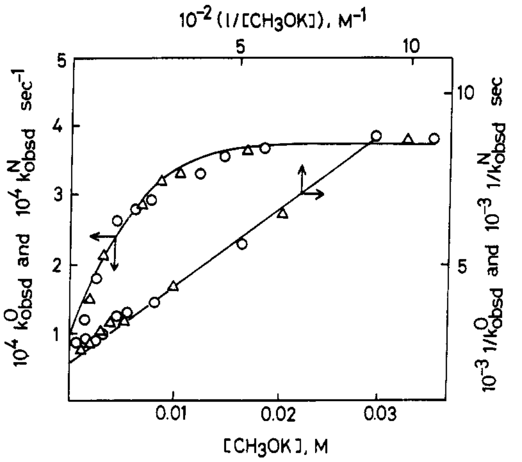

Figure 3. Relationships between K^O_{obsd} and k^N_{obsd} and [CH_3OK] and between $1/k^O_{obsd}$ and $1/k^N_{obsd}$ and 1/[CH_3OK] at 30 °C [μ = 0.05 M ($KClO_4$)]: (△) k^O_{obsd}; (○) k^N_{obsd}.

be dealt with as a fast mobile equilibrium. Accordingly, the following expression (eq 11) is obtained for the rate

$$k^O_{obsd} = \frac{k_4K_1K_2K_3[CH_3OK]}{1 + K_1K_2K_3K_5 + (K_1 + K_1K_2 + K_1K_2K_3)\ [CH_3OK]} \quad (11)$$

of the stage II reaction in the presence of excess CH_3OK, if the k_4 stage is rate determining and the K_5 and K_3 stages are mobile equilibria.

k^O_{obsd} is the pseudo-first-order rate constant for the rearrangement of **1e**.

Although the relationship between k^O_{obsd} and [CH_3OK] is curvilinear, the k^O_{obsd} would asymptotically approach a fixed value at higher [CH_3OK] (eq 12). Furthermore,

$$k^O_{obsd} = \frac{k_4K_2K_3}{1 + K_2 + K_2K_3} \quad (12)$$

if $(K_1 + K_1K_2 + K_1K_2K_3)[CH_3OK] \gg 1 + K_1K_2K_3K_5$, eq 12 would hold, and k^O_{obsd} would be independent of [CH_3OK]. This is the case with the results of preliminary work on the reaction of **1e** with sodium isopropoxide in the Me_2SO–2-propanol mixture (20:80, v/v).[12]

Moreover, taking the reciprocals of both sides of eq 11, one can derive the following expression (eq 13). As a

$$\frac{1}{k^O_{obsd}} = \frac{1 + K_1K_2K_3K_5}{k_4K_1K_2K_3[CH_3OK]} + \frac{(1 + K_2 + K_2K_3)}{k_4K_2K_3} \quad (13)$$

result, the plot of $1/k^O_{obsd}$ vs. 1/[CH_3OK] would be linear (Figure 3). The results in Figure 3 are compatible with eq 11 and 13.

Rearrangement of *N*-Acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (6e). In the rearrangement of **6e**, the process **6e** ⇄ **4e** ⇄ **3e** (Scheme III, eq 6 and 7) is very fast, and the process **3e** ⇄ **4e** → **5e** is relatively slow.[11] Therefore, in the treatment of the kinetics of the stage II reaction for **6e** the process **6e** ⇄ **4e** ⇄ **3e** can be dealt with as a fast mobile equilibrium. Accordingly, the rate of the stage II reaction in the presence of excess CH_3OK can be expressed by eq 14, provided the k_4 stage is rate determining (k^N_{obsd} is the pseudo-first-order rate constant).

$$k^N_{obsd} = \frac{\dfrac{k_4}{K_5}[CH_3OK]}{1 + \left(\dfrac{1}{K_5}\right)\left(1 + \dfrac{1}{K_3}\right)[CH_3OK]} \quad (14)$$

Table II. Pseudo-First-Order Rate Constants (k^N_{obsd}) for the Rearrangement of *N*-Acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (6e) with Potassium Methoxide in a Me_2SO–CH_3OH Mixture (60:40, v/v)[a]

temp, °C	10^3[CH_3OK], M	$10^4k^N_{obsd}$, s^{-1}
30	1.15	1.15 ± 0.03
	2.04	1.80 ± 0.05
	4.09	2.61 ± 0.07
	6.10	2.83 ± 0.07
	7.45	2.94 ± 0.07
	12.2	3.34 ± 0.08
	14.9	3.64 ± 0.09
	18.3	3.73 ± 0.09
	35.2	3.78 ± 0.09
40	1.15	3.20 ± 0.08
	2.04	4.60 ± 0.12
	4.08	7.10 ± 0.13
	6.10	8.04 ± 0.13
	7.45	8.90 ± 0.14
	11.2	9.56 ± 0.24
	14.9	9.78 ± 0.23
	35.2	10.3 ± 0.25
50	2.10	13.8 ± 0.2
	2.63	15.3 ± 0.2
	4.20	19.7 ± 0.4
	6.30	21.9 ± 0.4
	8.40	22.3 ± 0.4
	10.5	23.6 ± 0.4
	15.8	25.9 ± 0.4
	42.0	26.5 ± 0.5

[a] $[\mathbf{6e}]_0 = 1.32 \times 10^{-5}$ M; μ = 0.05 M ($KClO_4$); the decrease in absorption at 580 nm was measured on a conventional spectrophotometer.

Equation 14 indicates that which increasing [CH_3OK], k^N_{obsd} would approach a fixed value (eq 14) asymptotically. Under the condition $(1/K_5)[1 + (1/K_3)][CH_3OK] \gg 1$, eq 15 is obtained, indicating that k^N_{obsd} is independent of

$$k^N_{obsd} = \frac{k_4K_3}{1 + K_3} \quad (15)$$

[CH_3OK]. This is the case with the reaction of **6e** with sodium isopropoxide in the Me_2SO–2-propanol mixture (20:80, v/v).[12] Table II shows the dependence of k^N_{obsd} on [CH_3OK], which is illustrated in Figure 3. Furthermore, by taking the reciprocals of both sides of eq 14, one can derive eq 16, indicating the linear dependence of $1/k^N_{obsd}$

$$\frac{1}{k^N_{obsd}} = \frac{K_5}{k_4[CH_3OK]} + \frac{1 + K_3}{k_4K_3} \quad (16)$$

on 1/[CH_3OK]. The results in Figure 3 are compatible with eq 14 and 16. Interestingly, the plots of eq 11 and 14 and plots of eq 13 and 16 coincide with each other within experimental error.

Discussion

Stage I. From K_1K_2 and $(K_2K_3)^{-1}$ (Table I) the equilibria (**1e** + CH_3O^- ⇄ **3e** + CH_3OH and **6e** + CH_3O^- ⇄ **3e** + CH_3OH) were found to lie considerably toward **3e** (anionic σ complex) at higher [CH_3OK].

Comparison of k_2K_1 with $k_{-3}K_5^{-1}$ clearly shows the difference in nucleophilicity of both amide and alkoxide ions (Table I): as the acidities of amides ($RCONH- \rightarrow RCON^- + H^+$) are generally higher than those of alcohols ($ROH \rightarrow RO^- + H^+$),[9,13,14] it can be assumed that $K_1 > K_5^{-1}$.

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Table III. Temperature Dependence of $(1 + K_2 + K_2K_3)/k_4K_2K_3$ and $(1 + K_3)/k_4K_3$

temp, °C	$(1 + K_2 + K_2K_3)/k_4K_2K_3$, s	$(1 + K_3)/k_4K_4$, s
30	2350 ± 90	2320 ± 190
40	800 ± 50	820 ± 70
50	340 ± 30	340 ± 20

Accordingly it follows that $k_{-3} \gg k_2$ because $k_{-3}K_5^{-1} \gg k_2K_1$. These results show that the negative charge on the amide nitrogen atom **2e** is delocalized over the acetyl group [$\text{-N}^-\text{COCH}_3 \leftrightarrow \text{-N=C(O}^-)\text{CH}_3$], and thus the nucleophilicity of the amide ion is decreased, whereas the negative charge is concentrated on the alkoxyl oxygen atom (**4e**).

Although the differences in the solvents are taken into account, the k_2K_1 values are fairly low compared with those in the reaction of **1e** with sodium isopropoxide in the Me_2SO–2-propanol mixture (20:80, v/v),[12] which may be attributed to the lower reactivity of methoxide ion (Table I).

Comparison of k_3 with k_{-2} is very interesting: in Table I $k_3 \gg k_{-2}$ in agreement with the results obtained in aromatic nucleophilic reactions of alkyl aryl ethers with amines[15] and supporting the experimental fact that no **1e**, which should be formed as shown in Scheme I, was found in the reaction of **6e** with CH_3OK.

Stage II. It is very interesting that the k^{O}_{obsd} and k^{N}_{obsd} vs. [CH_3OK] plots or their inversion plots coincide with each other (Figure 3). These results are considered to support Scheme I. From the intercepts in the inversion plots the parameters $(1 + K_2 + K_2K_3)/k_4K_2K_3$ and $(1 + K_3)/k_4K_3$ can be estimated, which represent the lower limits of the reciprocals of k^{O}_{obsd} and k^{N}_{obsd} (Table III).

From the coincidence of the inversion plots the following relations are derived (eq 17 and 18). In order for eq 17

$$\frac{1 + K_1K_2K_3K_5}{k_4K_1K_2K_3} = \frac{K_5}{k_4} \tag{17}$$

$$\frac{1 + K_2 + K_2K_3}{k_4K_2K_3} = \frac{1 + K_3}{k_4K_3} \tag{18}$$

to be valid, $K_1K_2K_3$ should be much greater than 1. It follows, therefore, that $k_3 \gg$ *ca.* 10^{-2}, because the K_1K_2 values are ca. 10^2. Therefore, the K_3 value is larger than that in the reaction of **6e** with sodium isopropoxide in the Me_2SO–2-propanol (20:80, v/v),[12] which would be attributable to the kinds of alcohols and compositions of mixed solvents.

As treatment of **1a–d** with alkoxides yields the rearranged products **5a–e**, it is expected that $K_2 \gg 1$.[9] Therefore, eq 18 holds.

From Table III the $k_4K_3/(1 + K_3)$ values are $(4.31 \pm 0.35) \times 10^{-4}$ (30 °C), $(1.22 \pm 0.10) \times 10^{-3}$ (40 °C), and $(2.94 \pm 0.17) \times 10^{-3}$ (50 °C) s^{-1}. These numbers approximately represent the k_4K_3 value, since K_3 is expected to be much small than 1.[12] Therefore, the rate constants of rearrangement ($1 \xrightarrow{\ominus} 5$) depend almost entirely on the decomposition stages of anionic σ complexs and are essentially independent of their formation stages. The smaller K_3 values should contribute to the relatively low rates of rearrangement.

Registry No. **1e**, 70320-89-7; **2e**, 90246-21-2; **3e**, 90269-12-8; **4e**, 90246-22-3; **5e**, 90246-23-4; **6e**, 87666-43-1.

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(2 + 2) and (2 + 4) Cycloadditions of Fluorinated Allenes

William R. Dolbier, Jr.,* and Conrad R. Burkholder

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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Various (2 + 2) and (2 + 4) cycloadditions of difluoroallene and fluoroallene are presented and discussed mechanistically. The results are interpreted as reinforcing the hypothesis that distinct, and at times competing, concerted (2 + 4) and nonconcerted (2 + 2) mechanisms are involved.

1,1-Difluoroallene (DFA) has been shown[1] to undergo regiospecific (2 + 4) cycloadditions with respect to DFA, with the C_2–C_3 bond being exclusively incorporated into the new ring, while, in contrast, little regioselectivity with respect to the diene component is observed. In comparison to its (2 + 4) behavior, the (2 + 2) cycloadditions of DFA exhibit a lack of regiospecifity with respect to the DFA and increased regioselectivity with respect to the other (2 + 2) component (Scheme I).[1]

Likewise, fluoroallene (MFA) has been reported to undergo (2 + 4) cycloadditions with similar regiochemical behavior (Scheme II).[2]

These results were interpreted as deriving from the involvement of distinct and, in the case of the acyclic dienes, competitive, concerted (2 + 4) and nonconcerted (2 + 2) mechanistic processes. We present, at this time, results from a number of additional (2 + 4) and (2 + 2) cycloadditions of fluorine-substituted allenes, results which we believe provide additional support for the hypothesis of distinct mechanisms for the two modes of reaction.

Results and Discussion

(2 + 4) Cycloadditions. A number of additional cycloaddition reactions of DFA were studied with the aim

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