

Aromatic Nucleophilic Substitution. 11.¹ Effects of Ortho Substituents on the Rates of the Smiles Rearrangements of (β -Acetylamino)ethyl 2-X-4-Y-6-Z-1-phenyl Ethers with Potassium Hydroxide in Aqueous Dimethyl Sulfoxide

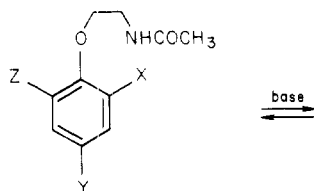
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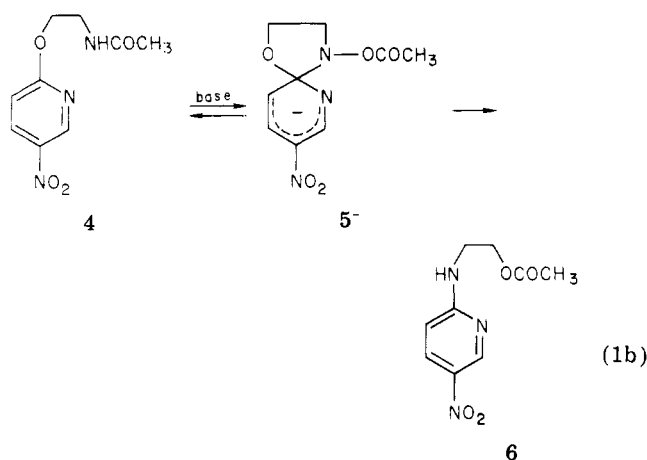
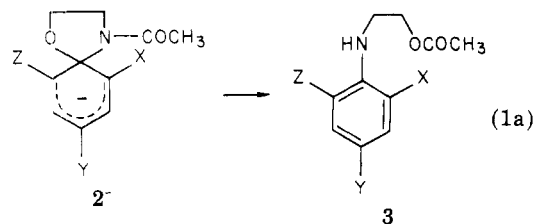
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β -(Acetylamino)ethyl 2-X-4-Y-6-Z-1-phenyl ether (**1d**, X = CH₃; Y = NO₂; Z = H; **1e**, X = Z = H; Y = NO₂) readily undergoes a Smiles rearrangement in aqueous Me₂SO in the presence of potassium hydroxide, giving *N*-(β -acetyloxy)ethyl- (**3**, main product) and *N*-(β -hydroxy)ethyl-2-X-4-nitro-6-Z-anilines. The ethers (**1d** and **1e**) rearrange more rapidly than **1a** (X = Y = NO₂, Z = H) by a factor of 55 and 1680, respectively, indicating that the steric effect plays an important role in the rearrangement. β -(Acetylamino)ethyl 2,6-dinitro-1-phenyl (**1f**, X = Z = NO₂; Y = H) and 2,4-dinitro-6-methyl-1-phenyl ethers (**1g**, X = Y = NO₂; Z = CH₃) rearrange much more slowly, giving stable anionic σ complexes.

In previous work³ we reported the kinetics of the base-catalyzed Smiles rearrangements of β -(acetylamino)ethyl 2-X-4-nitro-1-phenyl ethers (**1a-c**) and β -



- 1a**, X = Y = NO₂; Z = H
b, X = Br; Y = NO₂; Z = H
c, X = CN; Y = NO₂; Z = H



(acetylamino)ethyl 5-nitro-2-pyridyl ether (**4**) in Me₂SO-H₂O (96:4, v/v) and showed that for all the substrates studied the anionic σ complexes (**2**⁻ and **5**⁻, referred to as a σ complex) are spectrophotometrically

confirmed to intervene during the rearrangement course^{3,4} and that the rates of rearrangement depend only on the decomposition process of the complexes. The results are contrasted with many previous results.⁵⁻⁹ The effect of the 2-X group or the ring nitrogen atom is either steric or electronic, with the former factor predominating.

In order to obtain a closer insight into the mechanism, we have further synthesized β -(acetylamino)ethyl 2-methyl-4-nitro-1-phenyl (**1d**, X = CH₃; Y = NO₂; Z = H), β -(acetylamino)ethyl 4-nitro-1-phenyl (**1e**, X = Z = H; Y = NO₂), β -(acetylamino)ethyl 2,6-dinitro-1-phenyl (**1f**, X = Z = NO₂; Y = H), and β -(acetylamino)ethyl 2,4-dinitro-6-methyl-1-phenyl (**1g**, X = Y = NO₂; Z = CH₃) ethers and carried out the kinetics of their Smiles rearrangements.

This paper reports the comparison of these results with the previous ones³ and the comprehensive discussion about the mechanism of rearrangement.

Experimental Section

Capillary melting points are uncorrected. NMR spectra were recorded in Me₂SO with a Varian A-60D spectrometer according to the procedure described in the literature.¹⁰ Elemental analyses were performed at the Microanalytical Center of Gunma University. UV and visible spectra were measured in Me₂SO with a Hitachi-124 UV-vis spectrophotometer. Molecular extinction coefficients and absorption maxima were determined in Me₂SO. Chromatographic columns and TLC plates were prepared with Wako Gel-200 (silica gel) and B-10 (silica gel), respectively.

β -(Acetylamino)ethyl 2-Methyl-4-nitro-1-phenyl Ether (1d). 2-Methyl-4-nitrofluorobenzene (MNFB, bp 98–100 °C (13 mmHg)) was prepared at -15 °C from *o*-fluorotoluene and fuming nitric acid according to the procedure of Shiemann.¹¹ After 1.05 g (0.027 g-atom) of potassium had been added to 100 mL of dioxane containing 4.16 g (0.040 mol) of *N*-acetyethanolamine (NAEA) and the mixture had been refluxed such that the potassium was completely dissolved and brought to room temperature, 50 mL of dioxane containing 3.48 g (0.022 mol) of MNFB

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(2) The minus sign represents an ionic species.

(3) K. Okada and S. Sekiguchi, *J. Org. Chem.*, **43**, 441 (1978).

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(b) J. F. Bunnett and T. Okamoto, *J. Am. Chem. Soc.*, **78**, 5363 (1956);

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was added dropwise in the presence of 18-crown-6 ether (1 mL). After the mixture had been further stirred for 30 min, it was poured onto 200 mL of ice-water, neutralized with dilute HCl solution, extracted with chloroform, and dried over anhydrous Na_2SO_4 . After the chloroform had been distilled off and the residue had been submitted to column-chromatographic separation (silica gel-benzene), the raw material was recrystallized from benzene-ligroin to give 1.0 g of **1d** (18.7%, mp 120–122 °C); λ_{max} 325 nm (ϵ 1.06×10^4).

Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4$: C, 55.45; H, 5.92; N, 11.76. Found: C, 55.61; H, 6.07; N, 11.74.

β -(Acetylamino)ethyl 4-Nitro-1-phenyl Ether (1e). The ether (**1e**) was obtained in a 21% yield by use of *p*-nitrofluorobenzene according to the method used for **1d** (mp 119.6–120.5 °C); λ_{max} 316 nm (ϵ 1.14×10^4).

Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4$: C, 53.57; H, 5.39; N, 12.50. Found: C, 53.81; H, 5.54; N, 12.61.

β -(Acetylamino)ethyl 2,6-Dinitro-1-phenyl Ether (1f). Potassium 4-chloro-3,5-dinitrobenzenesulfonate (PCDS) was prepared from chlorobenzene, concentrated sulfuric acid (d 1.84), fuming sulfuric acid (ca. 25% free sulfur trioxide), and potassium nitrate according to the procedure described in the literature.¹² 2,6-Dinitroaniline (DNA) was prepared from PCDS and ammonium hydroxide according to the procedure described in the literature;¹² the total yield including the preparation of PCDS was 30%.

2,6-Dinitrochlorobenzene (DNCB) was prepared from DNA, sodium nitrite, concentrated sulfuric acid (d 1.84), and cuprous chloride according to the procedure described in the literature;¹³ the yield was 69%. 2,6-Dinitrofluorobenzene (DNFB) was prepared in 76% yield from DNCB and potassium fluoride according to the procedure of Parker and Read.¹⁴ The ether (**1f**) was prepared in a 13% yield from DNFB according to the method used for **1d** except for a reaction time of 5 min (mp 92–93 °C); λ_{max} 305 (sh) nm (ϵ 1.97×10^3). The maximum absorption band appears as a shoulder because of its overlapping with the absorption of Me_2SO .

Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_6$: C, 44.61; H, 4.12; N, 15.71. Found: C, 44.88; H, 4.22; N, 15.61.

β -(Acetylamino)ethyl 2,4-Dinitro-6-methyl-1-phenyl Ether (1g). Crude 2,4-dinitro-6-methylfluorobenzene was prepared in 89% yield from *o*-fluorobenzene, fuming nitric acid, and concentrated sulfuric acid (d 1.84) according to the procedure described in the literature¹⁵ and was submitted to the preparation of **1g** without further purification. The ether (**1g**) was prepared in a 10% yield according to the method used for **1d** (mp 109.5–110.5 °C).

Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_6$: C, 46.64; H, 4.63; N, 14.84. Found: C, 46.35; H, 4.54; N, 14.72.

***N*-(β -Acetyloxy)ethyl-2-methyl-4-nitroaniline (3d, X = CH_3 ; Y = NO_2 ; Z = H)**. After 0.747 mL (0.000769 mol) of *tert*-butanolic potassium *tert*-butoxide (1.03 N) had been added to 10 mL of Me_2SO containing 0.183 g (0.00077 mol) of **1d**, the mixture was stirred for 1 h at room temperature, acidified with 1.54 mL of HCl (1.00 N), poured into 60 mL of sodium chloride saturated water, and extracted twice with 50 mL of chloroform. After the chloroform solution (ca. 100 mL) had been dried over calcium chloride, the chloroform was evaporated off. TLC collection (silica gel) of the residue gave a rather pure product. Recrystallization of the product from ethanol gave 0.144 g (78.7%) of **3d** (mp 119.5–121 °C); λ_{max} 397 nm (ϵ 2.01×10^4).

Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4$: C, 55.45; H, 5.92; N, 11.76. Found: C, 55.73; H, 6.12; N, 11.92.

***N*-(β -Acetyloxy)ethyl-4-nitroaniline (3e, X = Z = H; Y = NO_2)**. After 30.9 g (0.506 mol) of ethanolamine had been added dropwise to a stirred solution of 150 mL of Me_2SO and 40.0 g (0.253 mol) of *p*-nitrochlorobenzene at 140 °C, the mixture was further stirred at the same temperature for 4 h, cooled, and poured onto 500 mL of ice-water. The crystals that formed [*N*-(β -hydroxy)ethyl-4-nitroaniline] were filtered with suction and dried, and then processed by the following procedure. After 3.37 g (0.033

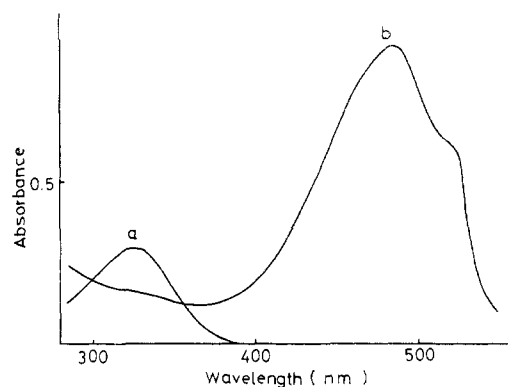


Figure 1. Absorption spectra relevant to the reaction of **1d** with *tert*-butanolic $\text{KOC}(\text{CH}_3)_3$ in Me_2SO : (a) **1d** (2.69×10^{-5} M); (b) immediately after addition of 50 equiv of $\text{KOC}(\text{CH}_3)_3$.

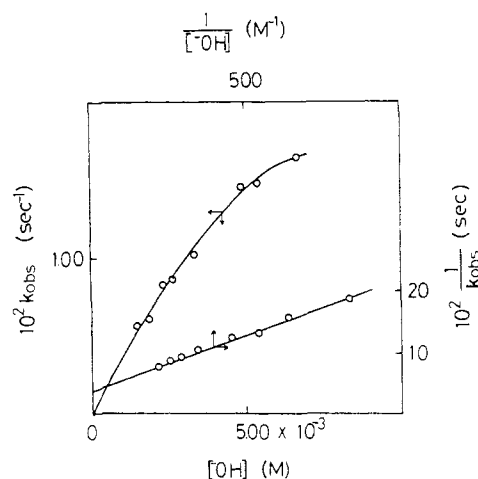


Figure 2. Relationships between k_{obs} and $[\text{OH}^-]$ and between $1/k_{\text{obs}}$ and $1/[\text{OH}^-]$ in the reaction of **1d** with KOH in 96% Me_2SO : $[\text{1d}]_0 = 2.6 \times 10^{-5}$ M; $\mu = 0.1$ (KClO_4).

mol) of acetic anhydride had been added dropwise at room temperature to a stirred, 100-mL, ethanol solution containing 2.0 g of the crystals and the mixture was stirred for 1 week at the same temperature, the solution was poured onto 300 mL of ice-water. The formed crystals were subjected to chromatographic separation (silica gel-benzene) and recrystallization from ethanol gave 0.5 g of **3e** (6.6% based on *p*-nitrochlorobenzene, mp 122.0–123.5 °C); λ_{max} 395 nm (ϵ 30 900).

Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4$: C, 53.57; H, 5.39; N, 12.50. Found: C, 53.38; H, 5.21; N, 12.21.

Kinetic Measurements. In kinetic measurements, KOH was used as a base, and the ionic strength was kept at 0.1 M (KClO_4). A mixture of Me_2SO - H_2O (96:4 v/v) was used as a solvent throughout all runs. Runs were set up so that KOH was in large excess over the substrate, which assured good pseudo-first-order kinetics. Rate constants at 25 °C were calculated by monitoring the increase in absorbance at 485 and 483 nm for **1d** and **1e**, respectively, which are attributable to **3d**⁻ and **3e**⁻ and at which wavelengths the reactants were transparent. The species [**3d**⁻, λ_{max} 485 nm (ϵ 31 800); **3e**⁻, λ_{max} 483 nm (ϵ 31 400)] are the anilide ions formed by removal of the amino protons of **3d** and **3e** with excess KOH. In the case of **1e**, the rates at 35 and 40 °C were measured with a Union RA-1200 rapid-reaction analyzer (Union Giken Co. Ltd.).

Results

General Features. The reaction of **1d** or **1e** with 50 equiv of *tert*-butanolic $\text{KOC}(\text{CH}_3)_3$ (0.64 N) in Me_2SO at room temperature gives **3d** or **3e** in a quantitative yield. Spectral change occurs upon addition of $\text{KOC}(\text{CH}_3)_3$ to a Me_2SO solution of **1d** (Figure 1). The spectrum (curve b) is attributed to **3d**⁻, because the reaction of **3d** with $\text{KOC}(\text{CH}_3)_3$ gives the same spectrum as curve b under the

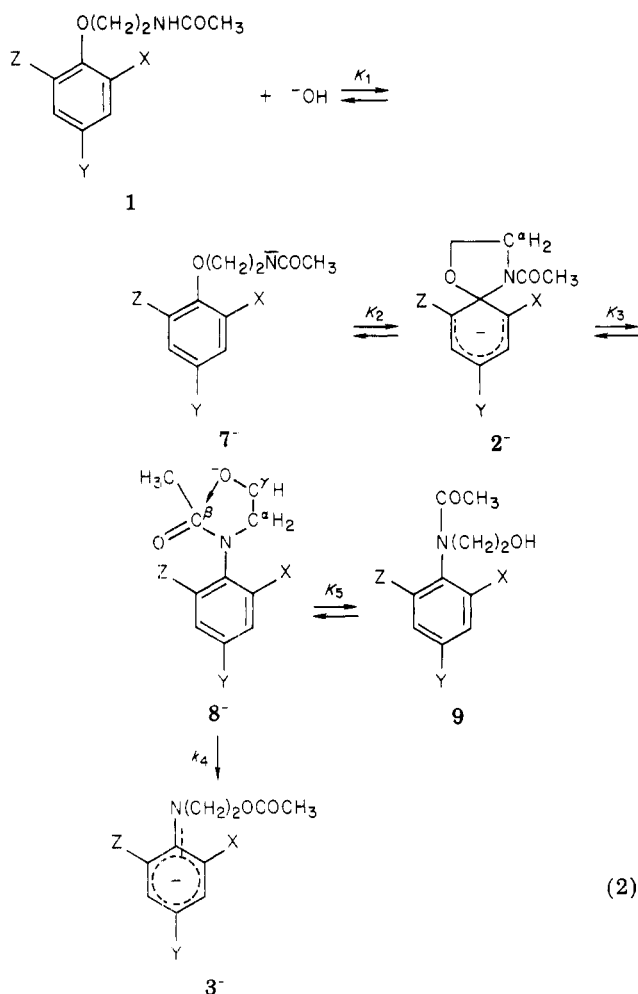
(12) *Org. Synth.*, **31**, 45 (1950).

(13) *Org. Synth.*, **32**, 23 (1950).

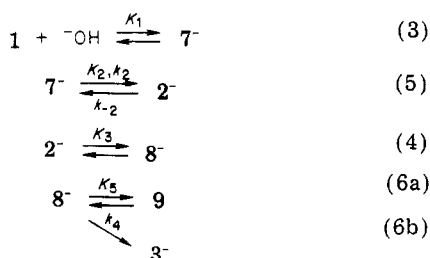
(14) R. E. Parker and T. O. Read, *J. Chem. Soc.*, 3149 (1962).

(15) R. Nietzki and E. Rehe, *Ber.*, **25**, 3005 (1892).

Scheme I



Scheme II



same condition. A similar spectral change was found in the case of **1e**. Although the spectrum due to an anionic σ complex was obtained in the case of **1a-c** and **4**, in the case of **1d** and **1e** no distinct spectra due to their complexes were found, indicating the instabilities of the complexes as will be discussed later.

Rearrangement. The apparent rate constants of rearrangement of **1d** and **1e** are summarized in Table I. Figure 2 shows the dependence of k_{obsd} upon $[\text{OH}^-]$ and $1/[\text{OH}^-]$, respectively.

As previously shown,³ the rearrangement proceeds according to Scheme I ($Z = \text{H}$). We rewrite Scheme I in a fashion more useful for quantitative discussions in Scheme II.

According to the procedure described in previous work,³ the rate of rearrangement is generally shown as follows:

$$\text{rate} = k_{\text{obsd}}[1]_{\text{st}} = \frac{k_4 K_1 K_2 K_3 [\text{OH}^-][1]_{\text{st}}}{1 + K_1 K_2 K_3 K_5 + (K_1 + K_1 K_2 + K_1 K_2 K_3)[\text{OH}^-]} \quad (7)$$

Rearranging eq 7, one can derive

$$\frac{1}{k_{\text{obsd}}} = \frac{1 + K_1 K_2 K_3 K_5}{k_4 K_1 K_2 K_3 [\text{OH}^-]} + \frac{1 + K_2 + K_2 K_3}{k_4 K_2 K_3} \quad (8)$$

Equation 8 is consistent with the rate data (Figure 2). Therefore, by the interpolation of $1/[\text{OH}^-]$ to the intercept in the linear plot of $1/k_{\text{obsd}}$ against $1/[\text{OH}^-]$ (eq 8), equation 9 is obtained (i means k_{obsd} at $1/[\text{OH}^-] \rightarrow 0$, that is, $[\text{OH}^-] \rightarrow \text{infinity}$). Relative rate data shown in Table I represent the ratio of k^i_{obsd} .

$$k^i_{\text{obsd}} = \frac{k_4 K_2 K_3}{1 + K_2 + K_2 K_3} \quad (9)$$

Anionic σ Complexes from **1f and **1g**.** It was observed by NMR spectroscopy that the addition of an equivalent of $\text{KOC}(\text{CH}_3)_3$ to a Me_2SO solution of **1f** and **1g** immediately gives the anionic σ complexes (**2f**⁻ and **2g**⁻) and that the spectra due to the complexes did not change after a long interval (17 h for **2f**⁻ and 24 h for **2g**⁻). The postulated structures of **2f**⁻ and **2g**⁻ are supported by a comparison of their spectra with those of similar complexes (Table II¹⁶). The complex **2g**⁻ resembles **12**⁻ and **2a**⁻ in their signal patterns in spite of the presence of a methyl group at the 6 position.

Discussion

Rate of Rearrangement. Table III shows the activation parameters and relative ratios, including those of **1a-c** and **4** for comparison. In the case of **1a-c** and **4** $K_2 \gg 1, 3$ so eq 9 is simplified to eq 10, which means that the

$$k^i_{\text{obsd}} = \frac{k_4 K_3}{1 + K_3} \quad (10)$$

rate of rearrangement depends only on the decomposition of an anionic σ complex, independent of its formation. On the other hand, in the case of **1d** and **1e**, the rate of rearrangement depends not only on the decomposition of the complex but also on its formation (eq 9). As shown in General Features, the anionic σ complexes are not stable. As a result, the potential energy barrier for the formation of complex is expected to be higher than in the case of **1a-c**. This means that K_2 is smaller. The ethers (**1d** and **1e**) with a methyl group and a hydrogen atom at the 2 position of the ring, respectively, undergo the Smiles rearrangements more rapidly than **1a**, being quite different from the results of Galbraith and Smiles.²⁰

It is not reasonable that one should discuss the activation parameters for all the substrates studied in the mass (Table III), since in the case of the first group consisting of **1a-c** and **4** the rate of rearrangement is expressed by eq 10, whereas that of the second group consisting of **1d** and **1e** is expressed by eq 9, which contains an additional constant, K_2 .

In the former group, the exception is the case of **4**, which is the result of the stereoelectronic effect of the nitrogen atom in a pyridine ring.³ In the latter group, the activation parameters compensate each other, indicating that the rearrangement proceeds under the same mechanism.

A molecular model shows that with **1e** the entropy loss would be greater to some extent in the K_2 stage than with **1d**, since the rotation about the bond of C_1 -ether oxygen

(16) See paragraph concerning supplementary material at the end of this paper. References 17, 18, and 19 are cited in Table II.

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Table I. Kinetic Data Relevant to the Rearrangement^a

| substrate | temp, °C | 10 ³ [KOH], M | <i>k</i> _{obsd} , ^b s ⁻¹ | rel. ^c rate (25 °C) | Δ <i>H</i> [‡] , kcal mol | Δ <i>S</i> [‡] , eu | |
|-----------------|-------------------------|--------------------------|---|-----------------------------------|------------------------------------|------------------------------|-------------------------|
| 1a ^d | 20 | 6.0 | 3.28 × 10 ⁻⁴ | 1 | 16.6 | -18.1 | |
| | | 1.2 | 5.84 × 10 ⁻⁴ | | | | |
| | 2.0 | 5.71 × 10 ⁻⁴ | | | | | |
| | 2.4 | 5.76 × 10 ⁻⁴ | | | | | |
| | 3.2 | 5.60 × 10 ⁻⁴ | | | | | |
| | 4.0 | 5.94 × 10 ⁻⁴ | | | | | |
| | 30 | 6.0 | 8.43 × 10 ⁻⁴ | | | | |
| | 40 | 6.0 | 2.16 × 10 ⁻³ | | | | |
| 1d | 25 | 1.2 | 5.82 × 10 ⁻³ | 55 | 18.6 | -3.0 | |
| | | 1.6 | 7.19 × 10 ⁻³ | | | | |
| | | 2.4 | 9.56 × 10 ⁻³ | | | | |
| | | 3.2 | 1.20 × 10 ⁻² | | | | |
| | | 4.0 | 1.38 × 10 ⁻² | | | | |
| | | 4.8 | 1.48 × 10 ⁻² | | | | |
| | | 6.0 | 1.71 × 10 ⁻² | | | | |
| | | 30 | 1.2 | | | | 7.72 × 10 ⁻³ |
| | 30 | 1.6 | 9.86 × 10 ⁻³ | | | | |
| | | 2.0 | 1.19 × 10 ⁻² | | | | |
| | | 2.4 | 1.36 × 10 ⁻² | | | | |
| | | 3.2 | 1.67 × 10 ⁻² | | | | |
| | | 4.0 | 1.92 × 10 ⁻² | | | | |
| | | 35 | 1.2 | | | | 1.17 × 10 ⁻² |
| | | 35 | 1.6 | | | | 1.54 × 10 ⁻² |
| | | | 2.4 | | | | 2.15 × 10 ⁻² |
| | 3.2 | | 2.70 × 10 ⁻² | | | | |
| | 4.0 | | 3.09 × 10 ⁻² | | | | |
| | 4.8 | | 3.52 × 10 ⁻² | | | | |
| | 6.0 | | 4.03 × 10 ⁻² | | | | |
| | 40 | | 1.2 | | | | 1.62 × 10 ⁻² |
| | 40 | | 1.6 | | | | 2.08 × 10 ⁻² |
| | | 2.0 | 2.47 × 10 ⁻² | | | | |
| | | 2.4 | 2.85 × 10 ⁻² | | | | |
| | | 3.2 | 3.56 × 10 ⁻² | | | | |
| | | 4.0 | 4.23 × 10 ⁻² | | | | |
| | | 6.0 | 5.39 × 10 ⁻² | | | | |
| | | 1e | 25 | | | | 1.2 |
| 1.6 | | | | 4.22 × 10 ⁻² | | | |
| 2.0 | 5.25 × 10 ⁻² | | | | | | |
| 2.4 | 6.31 × 10 ⁻² | | | | | | |
| 3.2 | 8.37 × 10 ⁻² | | | | | | |
| 4.0 | 1.00 × 10 ⁻¹ | | | | | | |
| 4.8 | 1.13 × 10 ⁻¹ | | | | | | |
| 6.0 | 1.26 × 10 ⁻¹ | | | | | | |
| 30 | 1.2 | | 5.02 × 10 ⁻² | | | | |
| 30 | 1.6 | | 6.59 × 10 ⁻² | | | | |
| | 2.0 | | 8.22 × 10 ⁻² | | | | |
| | 2.4 | | 9.85 × 10 ⁻² | | | | |
| | 3.2 | | 1.29 × 10 ⁻¹ | | | | |
| | 4.0 | | 1.56 × 10 ⁻¹ | | | | |
| | 35 | | 1.2 | 1.02 × 10 ⁻¹ | | | |
| | 35 | | 1.6 | 1.38 × 10 ⁻¹ | | | |
| | | 2.0 | 1.71 × 10 ⁻¹ | | | | |
| 2.4 | | 2.12 × 10 ⁻¹ | | | | | |
| 3.2 | | 2.78 × 10 ⁻¹ | | | | | |
| 4.0 | | 3.31 × 10 ⁻¹ | | | | | |
| 4.8 | | 3.84 × 10 ⁻¹ | | | | | |
| 6.0 | | 3.93 × 10 ⁻¹ | | | | | |
| 40 | | 1.6 | 1.53 × 10 ⁻¹ | | | | |
| 40 | 2.0 | 1.95 × 10 ⁻¹ | | | | | |
| | 2.4 | 2.32 × 10 ⁻¹ | | | | | |
| | 3.2 | 3.01 × 10 ⁻¹ | | | | | |
| | 4.0 | 3.73 × 10 ⁻¹ | | | | | |
| | 6.0 | 5.26 × 10 ⁻¹ | | | | | |

^a $\mu = 0.1$ (KClO₄); solvent 96% Me₂SO (v/v). [1a]₀ = 3.0 × 10⁻⁵; [1d]₀ = 2.6 × 10⁻⁵; [1e]₀ = 1.3 × 10⁻⁵ M. ^b All *k*_{obsd} are the average of at least triplicate measurements, their accuracy being within ±2.5%. ^c Ratio of *k*_{obsd}¹ (see text). The *k*_{obsd}¹ of 1a at 25 °C is 5.77 × 10⁻⁴ s⁻¹. ^d Cited from ref 3.

is freer in the former than in the latter, whereas in the *K*₃ stage the entropy gain would be much greater in the former than in the latter owing to the absence of repulsion between X(H) and C^αH₂ groups.³ Furthermore, with 1e the plane of C^β-N-C^α could be coplanar with the benzene plane in the *k*₄ stage, whereas it could not be coplanar with

1d.³ As a result, the composite effect would make Δ*S*[‡] become larger and positive in the case of 1e.

Effects of Ortho Groups. The ethers (1f and 1g) form the stable anionic σ complexes, which hardly undergo the Smiles rearrangements. For the decomposition of complex, that is, the rearrangement (*K*₃ and *k*₄ steps) to proceed as

Table III. Activation Parameters and Relative Rates Relevant to the Rearrangement^a

| sub- strate | rel rate (25 °C) | ΔH^\ddagger_{298} , kcal mol | ΔS^\ddagger_{298} , eu | ΔG^\ddagger_{298} , kcal mol |
|-----------------|---------------------|---|-----------------------------------|---|
| 1a ^b | 1 | 16.6 | -18.1 | 22.0 |
| 1b ^b | 62 | 16.0 | -11.5 | 19.4 |
| 1c ^b | 83 | 15.4 | -13.1 | 19.3 |
| 4 ^b | 1900 | 16.6 | -1.2 | 17.0 |
| 1d | 55 | 18.6 | -3.0 | 19.5 |
| 1e | 1680 | 21.3 | 12.9 | 17.5 |
| 1f | 0 | | | |
| 1g | 0 | | | |

^a Activation parameters were calculated on the basis of k^{obsd} at various temperatures. ^b Cited from the previous work.³

fast as possible, the C^β-N-C^α plane (eq 2) in 8⁻ must be coplanar with the benzene ring (for the detailed discussion, refer to ref 3). The molecular model, however, shows that the plane is almost perpendicular to the benzene ring in 8⁻, in the case of 1f or 1g.

On the other hand, the molecular model shows that in the case of 1f or 1g the C₁-O-CH₂ plane of 1 is appreciably

perpendicular to the benzene ring because of the restricted rotation about the C₁-O bond owing to the two ortho substituents. Therefore, 1f or 1g more easily forms the stable complex, where the O-C₁-N plane of 2⁻ is perpendicular to the benzene ring, the configuration releasing the steric strain at C₁ (sp³) the most.²¹

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Registry No. 1d, 70320-88-6; 1e, 22404-13-3; 1f, 70320-89-7; 1g, 70320-90-0; 2f⁻, 70343-40-7; 2g⁻, 70343-41-8; 3d, 70320-91-1; 3d⁻, 70320-92-2; 3e, 70320-93-3; 3e⁻, 70320-94-4; MNFB, 455-88-9; NAEA, 142-26-7; PCDS, 38185-06-7; DNA, 606-22-4; DNCB, 606-21-3; DNFB, 573-55-7; *p*-nitrofluorobenzene, 350-46-9; 2,4-dinitro-6-methylfluorobenzene, 348-97-0; *p*-nitrochlorobenzene, 100-00-5; *N*-(β-hydroxy)ethyl-4-nitroaniline, 1965-54-4.

Supplementary Material Available: Table of NMR chemical shifts for 1f, 2f⁻, 1g, 2g⁻, 10⁻, 11⁻, 12⁻, and 2a (1 page). Ordering information is given on any current masthead page.

(21) The detailed kinetics of the formation of spiro complex 8⁻ including 1a-c, 4, 1f, and 1g are now in progress.

Halogenated Ketenes. 32. The Cycloaddition of Dichloroketene with Silyl Enol Ethers

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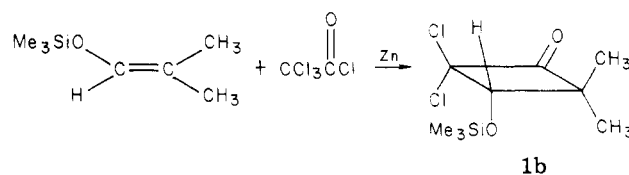
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The generation of dichloroketene by the zinc dechlorination of trichloroacetyl chloride in the presence of silyl enol ethers results in good yields of 2,2-dichloro-3-siloxycyclobutanones. The silyl substituent is easily removed to yield the 3-hydroxycyclobutanones. Several of the siloxycyclobutanones and 3-hydroxycyclobutanones were thermally unstable and underwent a silicon migration and ring-opening reaction to yield 1,1-dichloro-2,4-diones. This thermal instability is related to conformational effects in the cyclobutanone ring. The chlorine atoms on the 2,2-dichloro-3-siloxycyclobutanones are readily removed by tri-*n*-butyltin hydride reduction.

The cycloaddition of several ketenes with alkyl enol ethers has been reported to form 3-alkoxycyclobutanones in good yield.¹⁻³ The analogous reaction of dichloroketene with trimethylsilyl enol ethers has only recently been reported.^{4,5} We would like to report our findings on the cycloaddition of dichloroketene and a number of trimethylsilyl enol ethers and some chemistry of the resulting cyclobutanones.

The in situ cycloaddition of the trimethylsilyl enol ether from isobutyraldehyde, 1a, with dichloroketene generated from trichloroacetyl chloride by activated zinc in dry ether under a nitrogen atmosphere resulted in a 1:1 cycloadduct in 89% yield. A strong carbonyl absorption in the infrared at 1805 cm⁻¹ as well as other spectroscopic evidence

supported the siloxycyclobutanone 1b as the major product



of this reaction in accord with reported literature results.⁵ A number of other trimethylsilyl enol ethers were found to react smoothly with dichloroketene to give the 2,2-dichloro-3-(trimethylsilyloxy)cyclobutanones in good yield as revealed in Table I.

In most instances, the trimethylsilyl substituent was readily removed by dissolving the siloxycyclobutanone in methanol and stirring the solution for several hours. The methanol was evaporated and the 3-hydroxycyclobutanones were conveniently vacuum distilled. In this manner 1b gave 1c in 88% yield. In those instances where the removal of the trimethylsilyl substituent did not proceed readily, the addition of several drops of dilute acid

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