The Reaction of Nitrile Oxide–Quinone Cycloadducts. IV.[1] Acid-Catalyzed Dealkylative Aromatization of the 1 : 1 –C=C–Adducts and Base-Induced Rearrangement Products of Aromatic Nitrile Oxides with 2,5- and 2,6-Dialkyl-*p*-benzoquinones

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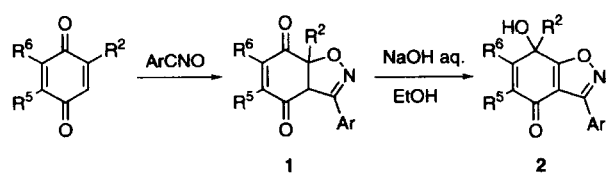
(Received October 14, 1999)

The 1,3-dipolar cycloadducts of aromatic nitrile oxides with 2,5- and 2,6-dialkyl-*p*-benzoquinones were treated with acetic anhydride/sulfuric acid to give isoxazole-fused hydroquinone diacetates in good yields. The base-induced rearrangement products from some of the 1,3-dipolar cycloadducts were treated with acetic anhydride/sulfuric acid to afford isoxazole-fused catechol diacetates and/or isoxazole-fused hydroquinone diacetates, depending on the slight difference in the substituents of the base-induced rearrangement products. The differences in the products are interpreted in terms of steric hindrance around the carbonyl and hydroxy moieties of the base-induced rearrangement products.

We have studied the 1,3-dipolar cycloaddition of aromatic nitrile oxides with various substituted *p*-benzoquinones. Results revealed that 2,5- and 2,6-dialkyl-*p*-benzoquinones afforded 1 : 1 –C=C–adducts, isoxazoline-fused cyclohexenedione derivatives **1** with aromatic nitrile oxides in excellent yields, with a small amount of 1 : 2-adducts in some cases.[2–4] Among the cycloadducts, those having a bulky substituent at the bridgehead position are found to undergo rearrangement with a base such as sodium hydroxide in an alcoholic solution to give isomeric compounds **2** in excellent yields (Scheme 1).[1] Since the cycloadducts have cyclohexenedione structure and the rearranged products possess 2,5-cyclohexadienone moiety, further rearrangement such as dienone–phenol rearrangement is expected to take place under an acidic condition. Dienone–phenol rearrangements of cyclohexadienones in acidic conditions have been widely investigated[5–7] and several types of rearrangement are known to take place depending on the reaction conditions and the substituents. So, we treated the 2,5-cyclohexadienone derivatives and also the cyclohexenedione derivatives with acetic anhydride/sulfuric acid. The structures of the products were determined and the reaction mechanisms were investigated.



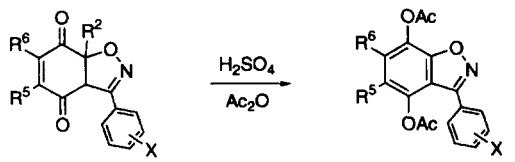
Scheme 1.

Results and Discussion

Reaction of Cycloadducts 1 with Acetic Anhydride/Sulfuric Acid. The reaction of the cycloadducts **1** with acetic anhydride/sulfuric acid was carried out; the results are shown in Table 1. While **1** has no cyclohexadienone moiety, **1** is isoxazoline-fused cyclohexenedione having *t*-butyl or isopropyl group at the bridgehead position. The substituent at the bridgehead position was eliminated during the reaction and isoxazole-fused hydroquinone diacetates **3** were obtained in good yields. The structure of **3b** was determined by X-ray crystallography; the ORTEP drawing is depicted in Fig. 1.

The reaction mechanism is thought to be like that shown in Scheme 2. At the initial stage of the reaction, one of the

Table 1. Reaction of Cycloadducts **1** with Acetic Anhydride/Sulfuric Acid



1 **3**

Entry	**1**	R^2	R^5	R^6	X	**3**	Yield/%[a]
1	**1a**	*t*-Bu	*t*-Bu	H	4-F	**3a**	88
2	**1b**	*t*-Bu	*t*-Bu	H	4-Cl	**3b**	82
3	**1c**	*t*-Bu	*t*-Bu	H	2,6-Cl_2	**3c**	85
4	**1d**	*t*-Bu	H	*t*-Bu	4-F	**3d**	88
5	**1e**	*t*-Bu	H	*t*-Bu	4-Cl	**3e**	86
6	**1f**	*t*-Bu	H	*t*-Bu	2,6-Cl_2	**3f**	90
7	**1g**	*i*-Pr	H	*i*-Pr	2,6-Cl_2	**3g**	89

a) Isolated yield.

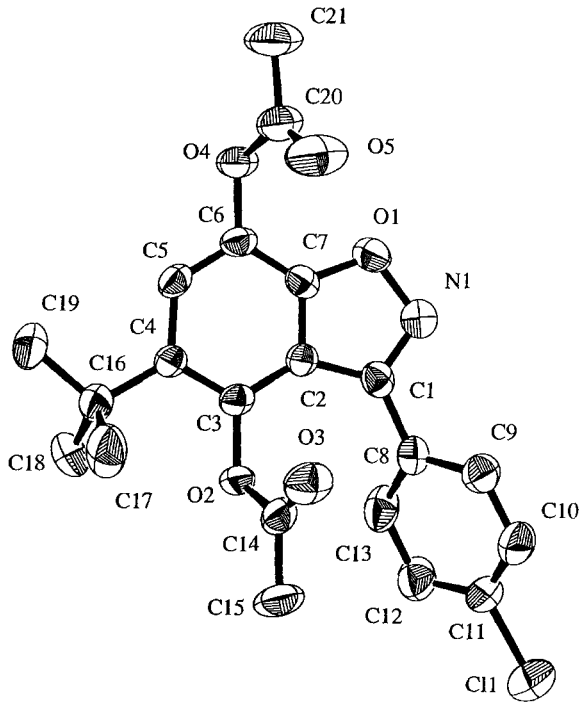
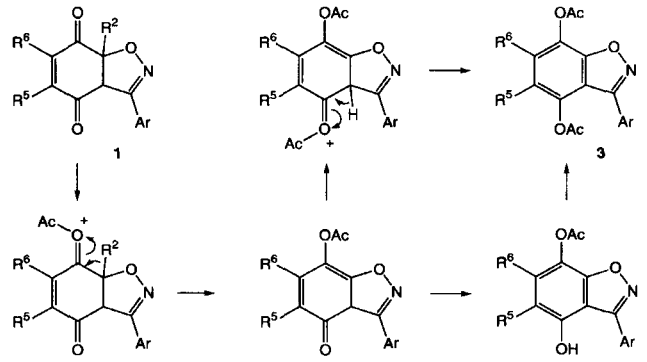


Fig. 1. ORTEP drawing of **3b**.



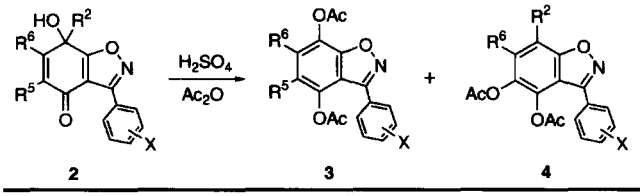
Scheme 2. Proposed mechanism of reaction of cycloadducts **1** with acetic anhydride/sulfuric acid.

carbonyl groups of **1** is attacked by acetyl cation to release *t*-butyl or isopropyl cation. At the second stage, the other carbonyl group is attacked in a similar manner and a proton is released, or isoxazole-fused hydroquinone monoacetate is formed by enolization and the hydroxy group is acetylated with acetyl cation. Thus the products **3** are formed. The eliminated alkyl cation may be trapped by acetic anhydride or acetate anion to give alkyl acetate. In the case of the reaction of **1g**, isopropyl acetate was found in the reaction mixture; however, *t*-butyl acetate was not detected in the cases of the reactions of **1a**—**f**. Any *t*-butyl cations released might be transformed into isobutene.

Reaction of Rearranged Products 2 with Acetic Anhydride/Sulfuric Acid. As reported before,[1] the nitrile oxide–quinone cycloadducts having a bulky substituent at the bridgehead position (R^2 = Et, *i*-Pr, Bn, and *t*-Bu in Scheme 1) undergo an unusual rearrangement with sodium hydroxide in ethanol to give rearranged products. The *p*-quinol derivatives **2** obtained by the base-induced rearrangement of the cycloadducts **1** were treated with acetic anhydride/sulfuric acid. The results are shown in Table 2.

The reaction of **2a** afforded a mixture of two different diacetates in the ratio of 75 : 25. The minor product was proved to be identical with **3a** from spectral data. The major product **4a** showed the same analytical data and had one *t*-butyl group, two acetyl groups, one aromatic proton, and one *p*-substituted benzene ring from ^{1}H NMR, showing it to be an isomer of **3a**. Similarly, **2b** afforded a mixture of **3b** and **4b** in the ratio of 15 : 85. The reaction of **2c** afforded a single diacetate, the spectral data of which were quite different from those of **3c**. The single crystal of the product **4c** was obtained and the structure was determined by X-ray crystallography. The ORTEP drawing is depicted in Fig. 2. The product **4c** was proved to be an isoxazole-fused catechol diacetate and the *t*-butyl group neighboring to the carbonyl group in **2c** was substituted by an acetoxy group. On the other hand, the reaction of **2g** afforded **3g** as a sole product. Differentiation of the products can be explained as shown in Scheme 3. The slight difference in

Table 2. Reaction of Rearranged Products **2** with Acetic Anhydride/Sulfuric Acid



Entry	2	R^2	R^5	R^6	X	Product (ratio[a])	Yield/%[b]
1	**2a**	*t*-Bu	*t*-Bu	H	4-F	**3a+4a** (25 : 75)	88
2	**2b**	*t*-Bu	*t*-Bu	H	4-Cl	**3b+4b** (15 : 85)	82
3	**2c**	*t*-Bu	*t*-Bu	H	2,6-Cl_2	**4c**	85
4	**2g**	*i*-Pr	H	*i*-Pr	2,6-Cl_2	**3g**	89

a) Determined by ^{1}H NMR. b) Isolated yield.

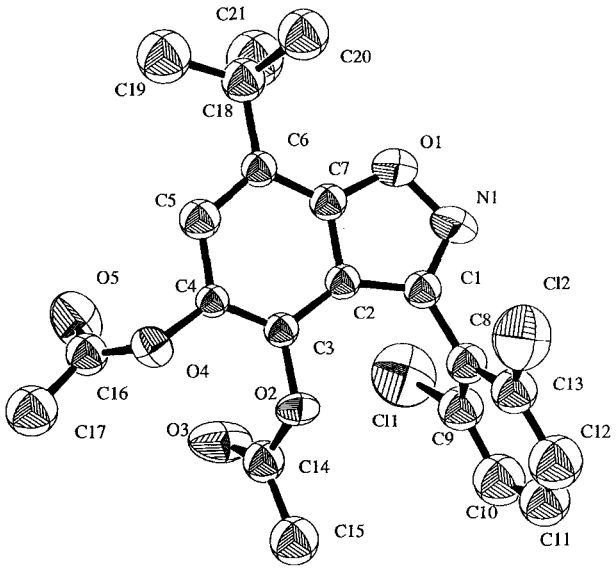
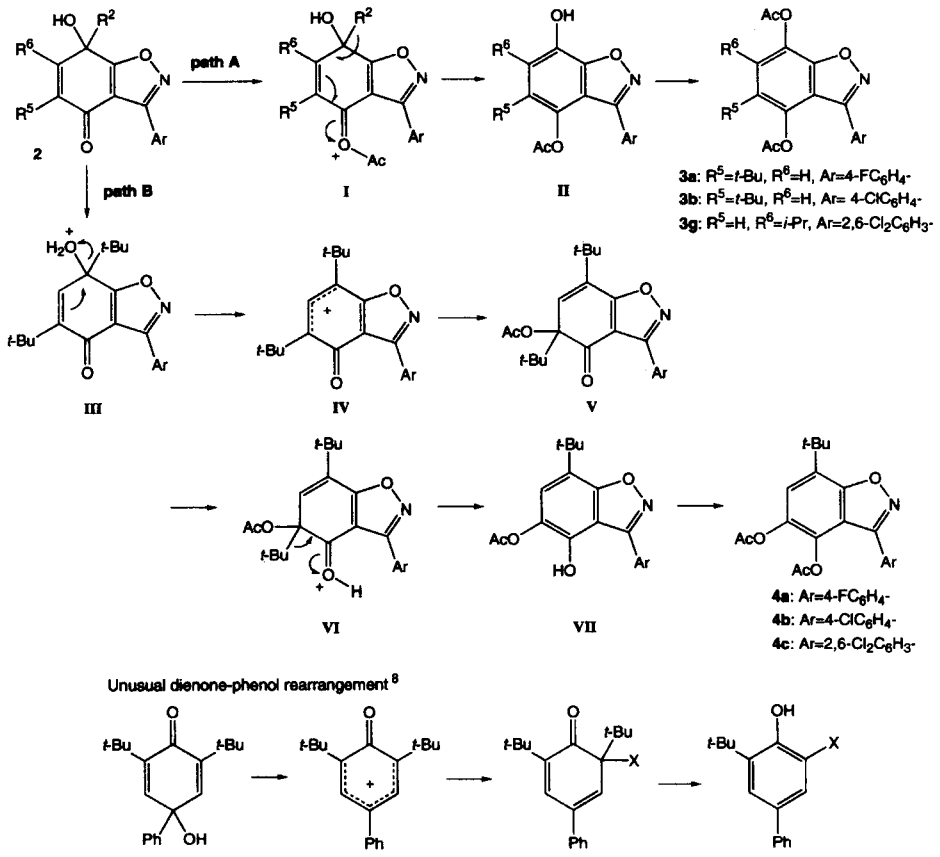


Fig. 2. ORTEP drawing of **4c**.



Scheme 3. Proposed mechanism of reaction of rearranged products **2** with acetic anhydride/sulfuric acid.

substituents caused a difference in the products. Usually, at the initial stage of a reaction of this type, carbonyl oxygen is attacked by acyl cation (almost the same as the case discussed for Scheme 2) to form a carbocation stabilized by extended conjugation, and then most labile cation is released to form phenol **II** (path A). If the carbonyl group is protected by adjacent bulky groups on either side, the acyl cation attack would be sterically hindered and the initial step would be protonation to hydroxy group and liberation of water to form carbocation **IV**, which is interrupted with acetate anion to form **V**. Protonation to carbonyl oxygen causes liberation of *t*-butyl group to form fully aromatic stable compound **VII**, subsequently acetylated to form the products **4** (path B). Thus, for **2g** (R^5 = H, Ar = 2,6-$Cl_2C_6H_3$–), only the mechanism via path A operates, and for **2c** (R^5 = *t*-Bu, Ar = 2, 6-$Cl_2C_6H_3$–), only the mechanism via path B operates. For **2a** and **2b** (R^5 = *t*-Bu, Ar = 4-XC_6H_4–), the mechanisms via both paths A and B operate but path B may dominate to form a larger amount of **4** than of **3** in the product mixtures. The mechanism via path B is very similar to that discussed in the unusual dienone–phenol rearrangement.[8]

In conclusion, we found that the reaction of the 1,3-dipolar cycloadducts **1** and their rearranged products **2** with acetic anhydride/sulfuric acid afforded isoxazole-fused hydroquinone diacetates **3** and/or isoxazole-fused catechol diacetates **4** by dealkylative aromatization. In the dienone–phenol rearrangement of cyclohexadienones having a *t*-butyl group, the elimination of the *t*-butyl group is known to occur.[9—12] Also, in our case, the *t*-butyl or isopropyl group was easily eliminated as cation in the acidic condition and aromatization took place to give **3** and/or **4**.

Experimental

General. Melting points were measured with Yazawa micro melting point measuring apparatus type BY-1 and were uncorrected. IR spectra were measured with a JASCO IR-700 spectrometer. ^{1}H NMR (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were measured with a JEOL JNM GX-270 spectrometer in chloroform-*d* and chemical shifts were reported in ppm from internal tetramethylsilane. Acetic anhydride and sulfuric acid were obtained from commercial sources and used without further purification.

Preparation of Cycloadducts 1 of *p*-Benzoquinones with Aromatic Nitrile Oxides. The cycloadducts **1b**, **1c**, **1f**, and **1g** were prepared according to the previous paper.[2] The other cycloadducts were prepared by a similar procedure.

1a: Yield 50%, yellow needles, mp 137—139 °C; IR (KBr) 3064, 2964, 2870, 1691 (C=O), 1604, 1512, 1479, 1371, 1327, 1236, 1158, 841 cm^{-1}; ^{1}H NMR δ = 1.05 (s, 9H), 1.13 (s, 9H), 4.83 (s, 1H), 6.73 (s, 1H), 7.07 (dd, J_{HH} = 9 Hz, J_{HF} = 9 Hz, 2H), 7.66 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 2H); ^{13}C NMR δ = 25.4, 28.4, 35.4, 36.4, 63.7, 96.8, 115.9 (d, $^2J_{CF}$ = 22 Hz), 124.0 (d, $^4J_{CF}$ = 3 Hz), 129.6 (d, $^3J_{CF}$ = 8 Hz), 137.9, 154.2, 160.6, 164.0 (d, $^1J_{CF}$ = 252 Hz), 193.5, 194.9. Found: C, 70.69; H, 6.87; N, 4.08%. Calcd for $C_{21}H_{24}FNO_3$: C, 70.57; H, 6.77; N, 3.92%.

1d: Yield 42%, yellow needles, mp 139—141 °C; IR (KBr) 3056, 2970, 2912, 2870, 1688 (C=O), 1596, 1469, 1370, 1344, 1246, 1090, 900, 858, 830 cm^{-1}; ^{1}H NMR δ = 1.10 (s, 9H), 1.27 (s, 9H), 4.73 (s, 1H), 6.54 (s, 1H), 7.08 (dd, J_{HH} = 9 Hz, J_{HF} = 9

Hz, 2H), 7.77 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 2H); ^{13}C NMR δ = 25.6, 29.0, 36.2, 36.6, 61.1, 96.9, 115.7 (d, $^{2}J_{CF}$ = 22 Hz), 123.9 (d, $^{4}J_{CF}$ = 4 Hz), 129.9 (d, $^{3}J_{CF}$ = 9 Hz), 134.1, 153.5, 164.0 (d, $^{1}J_{CF}$ = 253 Hz), 165.7, 190.7, 195.4. Found: C, 70.53; H, 6.93; N, 4.01%. Calcd for $C_{21}H_{24}FNO_3$: C, 70.57; H, 6.77; N, 3.92%.

1e: Yield 46%, pale yellow needles, mp 151—152 °C; IR (KBr) 2964, 2910, 2874, 1687 (C=O), 1597, 1370, 1245, 1090, 900, 858, 830 cm^{-1}; ^{1}H NMR δ = 1.10 (s, 9H), 1.27 (s, 9H), 4.73 (s, 1H), 6.54 (s, 1H), 7.37 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H); ^{13}C NMR δ = 25.2, 28.5, 35.8, 36.2, 60.4, 96.6, 125.7, 128.3, 128.6, 133.7, 136.2, 153.1, 165.2, 190.2, 194.8. Found: C, 67.28; H, 6.29; N, 3.79%. Calcd for $C_{21}H_{24}ClNO_3$: C, 67.46; H, 6.47; N, 3.75%.

Preparation of Base-Induced Rearrangement Products 2 of the Cycloadducts. The rearranged products **2b**, **2c**, and **2g** were prepared according to the previous paper.[3] Product **2a** was prepared by a similar procedure.

2a: Yield 92%, colorless needles, mp 159—161 °C; IR (KBr) 3464 (OH), 2968, 2914, 2874, 1675 (C=O), 1603, 1522, 1445, 1364, 1226, 1161, 1087, 842 cm^{-1}; ^{1}H NMR δ = 1.09 (s, 9H), 1.30 (s, 9H), 2.75 (br, 1H), 6.68 (s, 1H), 7.17 (dd, J_{HH} = 9 Hz, J_{HF} = 9 Hz, 2H), 8.05 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 2H); ^{13}C NMR δ = 25.2, 29.6, 35.2, 40.0, 74.3, 114.0, 115.5 (d, $^{2}J_{CF}$ = 22 Hz), 123.2 (d, $^{4}J_{CF}$ = 4 Hz), 131.6 (d, $^{3}J_{CF}$ = 9 Hz), 140.0, 147.7, 159.0, 164.2 (d, $^{1}J_{CF}$ = 252 Hz), 179.2, 181.4. Found: C, 70.38; H, 6.76; N, 3.95%. Calcd for $C_{21}H_{24}FNO_3$: C, 70.57; H, 6.77; N, 3.92%.

General Procedure of the Reaction of Cycloadducts 1 with Acetic Anhydride/Sulfuric Acid. To a solution of a cycloadduct **1** (0.5 mmol) in acetic anhydride (3 ml) was added sulfuric acid (0.5 mmol). The mixture was stirred at room temperature for 24 h and then poured into water (30 ml) to precipitate a solid. The solid was collected by filtration and recrystallized from hexane/benzene to give **3**. The yields of the products are written in Table 1.

3a: Colorless needles, mp 205—207 °C; IR (KBr) 3080, 2994, 2972, 2878, 1782 (C=O), 1609, 1502, 1364, 1329, 1175, 1054, 895, 840, 616 cm^{-1}; ^{1}H NMR δ = 1.37 (s, 9H), 1.75 (s, 3H), 2.44 (s, 3H), 7.22 (dd, J_{HH} = 9 Hz, J_{HF} = 9 Hz, 2H), 7.41 (s, 1H), 7.64 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 2H); ^{13}C NMR δ = 20.4, 20.7, 30.7, 34.9, 115.7 (d, $^{2}J_{CF}$ = 22 Hz), 117.7, 122.9, 124.3 (d, $^{4}J_{CF}$ = 4 Hz), 131.1, 131.5 (d, $^{3}J_{CF}$ = 9 Hz), 137.7, 139.5, 154.5, 157.1, 163.7 (d, $^{1}J_{CF}$ = 250 Hz), 168.3, 168.6. Found: C, 65.51; H, 5.07; N, 3.79%. Calcd for $C_{21}H_{20}FNO_5$: C, 65.45; H, 5.23; N, 3.63%.

3b: Colorless needles, mp 228—230 °C; IR (KBr) 3080, 2996, 2964, 2876, 1782 (C=O), 1624, 1603, 1496, 1364, 1171, 1053, 893, 833, 609, 526 cm^{-1}; ^{1}H NMR δ = 1.37 (s, 9H), 1.76 (s, 3H), 2.44 (s, 3H), 7.42 (s, 1H), 7.50 (d, J = 8 Hz, 2H), 7.60 (d, J = 8 Hz, 2H); ^{13}C NMR δ = 20.5, 20.6, 30.6, 34.9, 117.6, 122.9, 126.6, 128.8, 130.7, 131.0, 136.2, 137.7, 139.4, 154.5, 157.0, 168.2, 168.6. Found: C, 62.59; H, 4.93; N, 3.42%. Calcd for $C_{21}H_{20}ClNO_5$: C, 62.77; H, 5.02; N, 3.49%.

3c: Colorless needles, mp 193—194 °C; IR (KBr) 2970, 1776 (C=O), 1487, 1435, 1370, 1353, 1327, 1174, 1042, 886, 782 cm^{-1}; ^{1}H NMR δ = 1.35 (s, 9H), 1.58 (s, 3H), 2.44 (s, 3H), 7.39—7.48 (m, 4H); ^{13}C NMR δ = 19.5, 20.7, 30.6, 34.8, 118.2, 123.0, 126.8, 127.7, 128.5, 131.1, 131.6, 138.0, 139.1, 152.9, 154.3, 168.1, 168.5. Found: C, 57.77; H, 4.39; N, 3.24%. Calcd for $C_{21}H_{19}Cl_2NO_5$: C, 57.81; H, 4.39; N, 3.21%.

3d: Colorless needles, mp 136—138 °C; IR (KBr) 3078, 2972, 2914, 2876, 1777 (C=O), 1633, 1605, 1526, 1501, 1483, 1413, 1370, 1209, 1175, 1052, 920, 843, 620, 562 cm^{-1}; ^{1}H NMR δ = 1.43 (s, 9H), 1.99 (s, 3H), 2.48 (s, 3H), 7.07 (s, 1H), 7.20 (dd, J_{HH} = 9 Hz, J_{HF} = 9 Hz, 2H), 7.72 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 2H); ^{13}C NMR δ = 20.5, 20.9, 30.2, 35.4, 114.2, 115.7 (d, $^{2}J_{CF}$ = 22 Hz), 116.5, 124.2 (d, $^{4}J_{CF}$ = 4 Hz), 130.7, 131.0 (d, $^{3}J_{CF}$ = 9 Hz), 140.3, 144.6, 156.4, 157.9, 163.9 (d, $^{1}J_{CF}$ = 250 Hz), 167.8, 168.5. Found: C, 65.38; H, 5.14; N, 3.80%. Calcd for $C_{21}H_{20}FNO_5$: C, 65.45; H, 5.23; N, 3.63%.

3e: Colorless needles, mp 114—116 °C; IR (KBr) 3080, 2962, 2876, 1778 (C=O), 1629, 1498, 1369, 1208, 1173, 1052, 913, 836, 576, 525 cm^{-1}; ^{1}H NMR δ = 1.43 (s, 9H), 2.02 (s, 3H), 2.48 (s, 3H), 7.08 (s, 1H), 7.49 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H); ^{13}C NMR δ = 20.6, 20.9, 30.3, 35.5, 114.1, 116.6, 126.5, 128.9, 130.4, 130.7, 136.4, 140.2, 144.8, 156.4, 157.9, 167.8, 168.6. Found: C, 62.54; H, 4.94; N, 3.53%. Calcd for $C_{21}H_{20}ClNO_5$: C, 62.77; H, 5.02; N, 3.49%.

3f: Colorless needles, mp 131—132 °C; IR (KBr) 3080, 2966, 1781 (C=O), 1632, 1502, 1429, 1372, 1178, 1044, 918, 876, 788 cm^{-1}; ^{1}H NMR δ = 1.43 (s, 9H), 1.74 (s, 3H), 2.48 (s, 3H), 7.10 (s, 1H), 7.38—7.50 (m, 3H); ^{13}C NMR δ = 19.7, 20.9, 30.3, 35.5, 114.8, 116.4, 126.9, 128.0, 130.7, 131.5, 136.3, 140.1, 144.7, 152.5, 157.5, 167.7, 168.2. Found: C, 57.72; H, 4.43; N, 3.36%. Calcd for $C_{21}H_{19}Cl_2NO_5$: C, 57.81; H, 4.39; N, 3.21%.

3g: A pale yellow powder, mp 143.5—145.5 °C; IR (KBr) 3074, 2968, 1773 (C=O), 1634, 1510, 1431, 1362, 1350, 1215, 1203, 1180, 1041, 884, 789, 778 cm^{-1}; ^{1}H NMR δ = 1.27 (d, J = 7 Hz, 6H), 1.73 (s, 3H), 2.48 (s, 3H), 3.24 (sep, J = 7 Hz, 1H), 7.02 (s, 1H), 7.38—7.51 (m, 3H); ^{13}C NMR δ = 19.8, 20.5, 23.0, 27.7, 114.5, 115.4, 126.9, 128.0, 129.0, 131.6, 136.3, 141.1, 144.0, 152.7, 156.8, 168.10, 168.14. Found: C, 57.06; H, 4.04; N, 3.50%. Calcd for $C_{20}H_{17}Cl_2NO_5$: C, 56.89; H, 4.06; N, 3.32%.

General Procedure of the Reaction of Base-Induced Rearrangement Products 2 with Acetic Anhydride/Sulfuric Acid. To a solution of a rearranged product **2** (0.5 mmol) in acetic anhydride (3 ml) was added sulfuric acid (0.5 mmol). The resulting mixture was stirred at room temperature for 24 h and then poured into water (30 ml) to precipitate a solid. The solid was collected by filtration and recrystallized from hexane/benzene to give **3**and/or **4**. The yields of the products are written in Table 2.

Reaction of Rearranged Products 2a and 2b: Solid products from **2a** and **2b** were subjected to ^{1}H NMR measurement and the product ratios **3a/4a** and **3b/4b** were determined by integration of the methyl proton in the ^{1}H NMR spectra. Recrystallization of the mixtures from acetonitrile/water afforded **3a** (**3b**) as colorless cubes and **4a** (**4b**) as colorless needles, respectively. The two different crystals were separated by hand-picking.

4a: Mp 112—113 °C; IR (KBr) 2964, 1770 (C=O), 1610, 1513, 1367, 1206, 1176, 1011, 952, 909, 887, 843, 579 cm^{-1}; ^{1}H NMR δ = 1.54 (s, 9H), 1.94 (s, 3H), 2.32 (s, 3H), 7.20 (dd, J_{HH} = 9 Hz, J_{HF} = 9 Hz, 2H), 7.24 (s, 1H), 7.70 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 2H); ^{13}C NMR δ = 20.0, 20.6, 29.5, 34.6, 115.49, 115.54 (d, $^{2}J_{CF}$ = 21 Hz), 122.3, 124.3 (d, $^{4}J_{CF}$ = 3 Hz), 131.0 (d, $^{3}J_{CF}$ = 8 Hz), 132.7, 133.1, 137.8, 156.4, 160.9, 163.6 (d, $^{1}J_{CF}$ = 250 Hz), 167.3, 168.4. Found: C, 65.34; H, 5.12; N, 3.78%. Calcd for $C_{21}H_{20}FNO_5$: C, 65.45; H, 5.23; N, 3.63%.

4b: Mp 139—140 °C; IR (KBr) 3076, 2966, 2874, 1788 (C=O), 1510, 1367, 1198, 1169, 1088, 1013, 955, 921, 882, 526 cm^{-1}; ^{1}H NMR δ = 1.54 (s, 9H), 1.96 (s, 3H), 2.32 (s, 3H), 7.25 (s, 1H), 7.49 (d, J = 9 Hz, 2H), 7.66 (d, J = 9 Hz, 2H); ^{13}C NMR δ = 20.0, 20.6, 29.4, 34.6, 115.5, 122.5, 126.8, 128.8, 130.4, 132.8, 133.2, 136.2, 137.9, 156.5, 161.1, 167.5, 168.6. Found: C, 62.47; H, 5.11; N, 3.32%. Calcd for $C_{21}H_{20}ClNO_5$: C, 62.77; H, 5.02; N, 3.49%.

Reaction of Rearranged Product 2c: Product **4c** was obtained exclusively as colorless needles.

Table 3. X-Ray Crystallographic Data for **3b** and **4c**

	3b	**4c**
Empirical formula	$C_{21}H_{20}ClNO_5$	$C_{21}H_{19}Cl_2NO_5$
Formula weight	401.85	436.29
Crystal dimension/mm	$0.2 \times 0.7 \times 0.6$	$0.05 \times 0.25 \times 0.9$
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a/Å	17.366(4)	12.901(2)
b/Å	11.771(2)	16.071(2)
c/Å	19.583(2)	11.293(2)
α/deg		108.25(1)
β/deg	93.80(1)	96.67(2)
γ/deg		80.55(1)
V/Å^3	3993.9(10)	2188.4(7)
Z	8	4
D_{calcd}/g cm^{-3}	1.336	1.324
μ(Mo $K\alpha$)/cm^{-1}	2.23	3.27
$F(000)$	1680	904
Scan method	$\omega/2\theta$	$\omega/2\theta$
Scan rate/deg min^{-1}	16	16
$2\theta_{max}$/deg	55	45
No. of unique reflections	4832	5712
Transmission factor	0.9534—0.9999	0.8859—0.9999
No. of data used	2009 ($I > 3\sigma(I)$)	1987 ($I > 3\sigma(I)$)
No. of variables	254	314
R; R_w	0.049; 0.029	0.076; 0.045
Goodness of fit indicator	2.74	2.42

4c: Mp 185—188 °C; IR (KBr) 2964, 1780 (C=O), 1520, 1431, 1370, 1351, 1201, 1178, 1087, 1010, 960, 892, 780 cm^{-1}; ^{1}H NMR δ = 1.56 (s, 9H), 1.71 (s, 3H), 2.28 (s, 3H), 7.26 (s, 1H), 7.41—7.51 (m, 3H); ^{13}C NMR δ = 19.3, 20.6, 29.7, 34.7, 116.3, 122.8, 127.3, 128.0, 131.5, 132.5, 133.2, 136.4, 138.1, 152.8, 160.8, 167.1, 168.5. Found: C, 57.83; H, 4.22; N, 3.36%. Calcd for $C_{21}H_{19}Cl_2NO_5$: C, 57.81; H, 4.39; N, 3.21%.

X-Ray Crystallographic Studies. Single crystals of **3b** and **4c** were obtained by recrystallization from hexane. Cell-parameter measurements and reflection data collection were carried out at room temperature on a Rigaku AFC 7R four-circle diffractometer using Mo $K\alpha$ radiation monochromated by graphite (λ = 0.71069 Å). The orientation matrices and unit cell parameters were derived from the least-squares fit of 22 ($35.0° < 2\theta < 38.9°$) for **3b** and 23 ($20.7° < 2\theta < 24.3°$) for **4c** machine-centered reflections. No significant decay in the intensities of the three standard reflections was observed during data collections. Intensity data were corrected for the Lorentz and polarization effects and for absorption (empirical, ψ scans). Crystallographic data are summarized in Table 3.

Structure solution and refinements were performed using the teXsan crystallographic software package.[13] The positions of the non-hydrogen atoms were determined by direct methods (SIR-88[14]) and subsequent Fourier syntheses. The carbon atoms of the *t*-Bu group of **4c** were refined isotropically. All other non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares techniques. The hydrogen atoms were placed at the calculated positions. All hydrogen atoms were included in the final stages of refinements with fixed parameters.

We thank Associate Professor Youichi Ishii of the University of Tokyo for his help in X-ray measurements. This work was supported by a Grant-in-Aid for Scientific Research-(B) No. 07455353 from the Ministry of Education, Science, Sports and Culture.

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