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Elimination of 3-Hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans to 2-Nitrobenzo[*b*]furans[1]

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β-Elimination of stereoisomeric *cis*- and *trans*-3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans was investigated. The 2,3-dihydrobenzo[*b*]furans were stable under acidic conditions but were easily dehydrated under basic conditions to afford the corresponding 2-nitrobenzo[*b*]furans. An $(E1cB)_R$ mechanism is proposed on the basis of several lines of evidence obtained from studies on kinetics, ultraviolet spectra, leaving group effect and deuterium isotope effect in the elimination reaction.

Keywords——3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furan derivative; elimination; $(E1cB)_R$ mechanism; kinetic study; carbanion intermediate; leaving group effect; isotope effect

Several 3-hydroxy(or acetoxy)-2,3-dihydrobenzo[*b*]furan derivatives are convertible to the corresponding benzo[*b*]furans in the presence of acid.[2a,b] The elimination reactions have been studied to elucidate the reaction mechanism and relation between reactivity and stereostructure of the 2,3-dihydrobenzo[*b*]furans. It was reported that *cis*-2-benzoyl-[3] and *cis*-2-phenyl-3-hydroxy-2,3-dihydrobenzo[*b*]furans[4] were dehydrated more rapidly than the *trans* isomers to give corresponding benzo[*b*]furans in the presence of HCl. Baciocchi *et al.* reported that the elimination reaction of 2,3-dichloro-2,3-dihydrobenzo[*b*]furan under acidic conditions proceeded *via* and *E*1 process.[5] On the other hand, under basic conditions, *cis*-2,3-diazido-[6] and *cis*-2,3-dihalo-2,3-dihydrobenzo[*b*]furans[7] were converted to the corresponding benzo[*b*]furans more rapidly than the *trans* isomers. This may be because eliminations from five- and six-membered rings involve preferred transition states in which the leaving groups are *anti* to one another.[8] Recently, the elimination mechanism of 2,3-dihalo-2,3-dihydrobenzo[*b*]furans in the presence of alkoxide was also reported.[9]

In the previous paper,[10] we reported the preparation and stereochemistry of several *cis*- and *trans*-3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furan derivatives which were convertible to antibacterially active 2-nitrobenzo[*b*]furans[11] by elimination of H_2O. We wished to elucidate the reaction pathway from the 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans to the 2-nitrobenzo[*b*]furans and the kinetics of the eliminations in the diastereoisomeric five-membered ring system.[1]

First attempts to achieve dehydration of *cis*- and *trans*-6-ethoxy-3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furan[10] (**1** and **2**) and *cis*- and *trans*-5-bromo-3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furan[10] (**3** and **4**) in the presence of HCl, H_2SO_4, H_3PO_4 or *p*-TsOH all resulted in the quantitative recovery of the starting materials. This might be owing to the presence of the 2-nitro group (Chart 1). Treatment of the 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans (**1**, **2**, **3** and **4**) with bases such as KOH, NaOH and CH_3ONa resulted in almost quantitative formation of the 2-nitrobenzo[*b*]furans. The mechanism of the dehydrative elimination was investigated in detail.

The reactions were monitored by ultraviolet (UV) spectrophotometry. When ethanolic

1 : $R_1=R_3=H$, $R_2=OC_2H_5$
3 : $R_1=Br$, $R_2=R_3=H$
7 : $R_1=Br$, $R_2=H$, $R_3=COCH_3$

2 : $R_1=R_3=H$, $R_2=OC_2H_5$
4 : $R_1=Br$, $R_2=R_3=H$
8 : $R_1=Br$, $R_2=H$, $R_3=COCH_3$

Chart 1

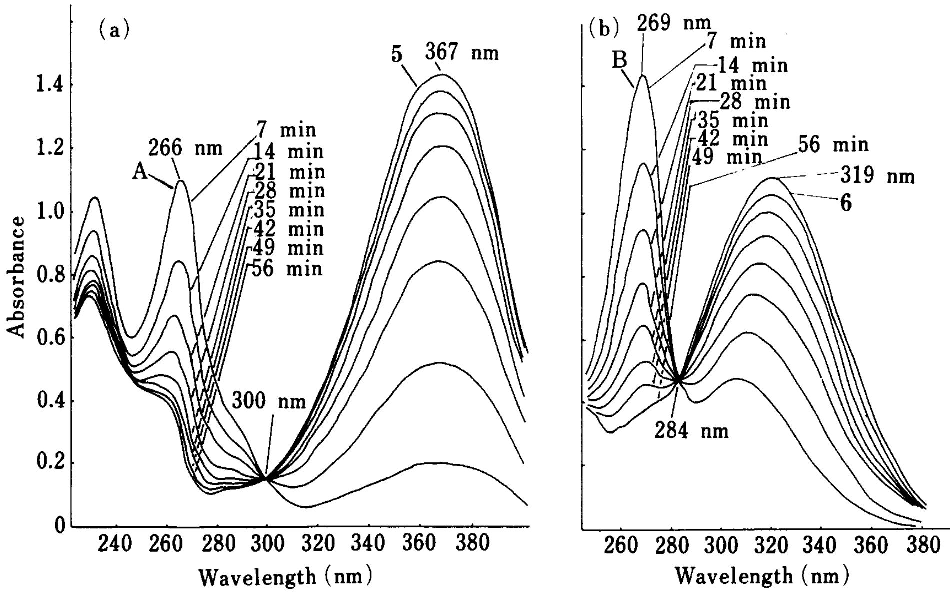

Fig. 1. UV Spectra of Mixtures of **1** and KOH (a), and of **3** and KOH (b)

solutions of 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans (**1** and **2**)[12] [$\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 283 (*ca.* 3450)] (8.88×10^{-5} M) were treated with a small excess of KOH (3.57×10^{-4} M), the UV spectra of the solutions showed a strong blue-shift [$\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 266 (*ca.* 20000)] (A in Fig. 1). These spectral features suggested that **1** and **2** are probably converted to the corresponding stable carbanion [conjugate anion (A)] under the conditions used (Chart 3).[13] Subsequently, the UV spectrum of the conjugate anion (A) changed slowly, finally becoming superimposable on that of 6-ethoxy-2-nitrobenzo[*b*]furan (**5**). Similar formation of the conjugate anion (B) [$\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 269 (*ca.* 20000)] from **3** and **4**[12] was also observed under the same conditions, and B was finally converted to 5-bromo-2-nitrobenzo[*b*]furan (**6**).[10] The elimination processes were monitored by continuously recording the UV spectra (Fig. 1). During the conversion of the conjugate anions (A and B) to the corresponding 2-nitrobenzo[*b*]furans (**5** and **6**), clear isosbestic points at 300 and 284 nm were observed, respectively, as shown in Fig. 1.

Kinetic determinations of the elimination reactions of 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans (**1**, **2**, **3** and **4**) to the 2-nitrobenzo[*b*]furans (**5**, **6**) were carried out by tracing the change of the UV spectra. Ethanolic solutions of **1** and **2** were placed in a flask equipped with a soda lime tube, and an ethanolic solution of KOH was added to each solution at 28.5 °C. The initial concentration of the substrate (**1**, **2**) was 10^{-5} M and the concentration of KOH was varied in the range of 10^{-4}—10^{-3} M in the reaction mixtures. Each reaction mixture was stirred at 28.5 °C and the progress of the reaction was checked for about 1 h by measurement of the decrease of absorbance ($\lambda_{266\,\mathrm{nm}} - \lambda_{305\,\mathrm{nm}}$)[14] at regular intervals with double-wavelength UV spectrometer. The rate constants of the reactions were calculated from the decrease of absorbance treated by the least-squares method. Kinetic experiments for **3** and **4** were also

TABLE I. Kinetic Data for the Elimination Reactions of *cis*- and *trans*-3-Hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans (**1**—**4**) *via* Conjugate Anions (A, B) in KOH–Ethanol at 28.5 °C

Run	Substrate	Concentration		k_2[a] ($\times 10^{-2}$, M^{-1}m^{-1})	r	Isosbestic point (nm)
		Substrate ($\times 10^{-5}$ M)	KOH (M)			
1	**1**	8.88	3.57×10^{-4}	4.81	0.9999	300
	2	8.88	3.57×10^{-4}	4.74	0.9997	300
2	**1**	8.80	3.54×10^{-3}	4.97	0.9996	300
	2	8.80	3.54×10^{-3}	5.01	0.9995	300
3	**3**	8.15	3.32×10^{-4}	1.96	0.9982	284
	4	8.15	3.32×10^{-4}	1.99	0.9980	284
4	**3**	8.17	2.33×10^{-3}	2.06	0.9996	284
	4	8.17	2.33×10^{-3}	2.08	0.9995	284

a) Average of at least two determinations.

carried out by measurement of the decrease of absorbance ($\lambda_{269\,\mathrm{nm}} - \lambda_{362\,\mathrm{nm}}$)[14] under similar conditions. These kinetic results are shown in Table I.

The results in Table I showed that the reaction rate constants of the *cis* isomers were nearly equal to those of the *trans* isomers. This suggested that the elimination proceeded *via* a pathway which was independent of the stereoisomerism of the substrates. When KOH was applied to the reaction at various concentrations over a range of about 10-fold, the rate constants were not changed at all (runs 1 and 2 in Table I). In addition, the kinetic plots of consumption of substrates against time exhibited excellent linearity ($r > 0.99$). These facts revealed that the elimination was first order in the substrate and was independent of the concentration of KOH.[15]

Thus, it is clear that the elimination mechanism of the 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans is different from that of 2,3-diazido- or 2,3-dihalo-2,3-dihydrobenzo[*b*]furans to the corresponding benzo[*b*]furans.[6,7] This prompted us to investigate in more detail the elimination process of the 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans.

Several examinations were carried out as follows in order to substantiate the involvement of the conjugate anions (A and B). After detecting production of the conjugate anion in the reaction mixture by UV spectroscopy, the mixture was neutralized immediately with 0.1 N HCl. The UV spectrum of the mixture coincided with that of the starting 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans. Russell[16] presented evidence to show the presence of stable carbanions by replacement of hydrogen with deuterium. The *trans* compound (**4**) was treated with KOD in C_2H_5OD, followed by treatment with DCl according to his procedure, to give a mixture consisting of crude *cis*- and *trans*-5-bromo-3-hydroxy[OD]-2-nitro-2,3-[2-D]dihydrobenzo[*b*]furan (**9** and **10**) (**9** : **10** ≒ 1 : 3). In addition, **1**, **2**, **3** and **4** were treated with CH_3OD for 24 h at 25 °C in the presence of a trace amount of KOD to give the corresponding 3-hydroxy[OD]-2-nitro-2,3-[2-D]dihydrobenzo[*b*]furans. These results demonstrated the existence and reversible formation of the conjugate anions from 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans in the initial stage of the elimination reactions.[17]

The leaving group effect was also examined by using *cis*- and *trans*-3-acetoxy-5-bromo-2-nitro-2,3-dihydrobenzo[*b*]furan (**7** and **8**), which were prepared from **3** and **4**, respectively, by treatment with acetic anhydride in the presence of H_2SO_4. Kinetic studies of the acetoxy compounds (**7** and **8**), having a good leaving group at 3-position, were carried out under the same conditions as the kinetic studies of **3** and **4**. In the experiments, both **7** and **8** gave **6** within 1.5 min. The rate constants of the hydroxy compounds (**3** and **4**) were about 2.1×10^{-2} M^{-1} m^{-1}, whereas those of the acetoxy compounds (**7** and **8**) were too large to be

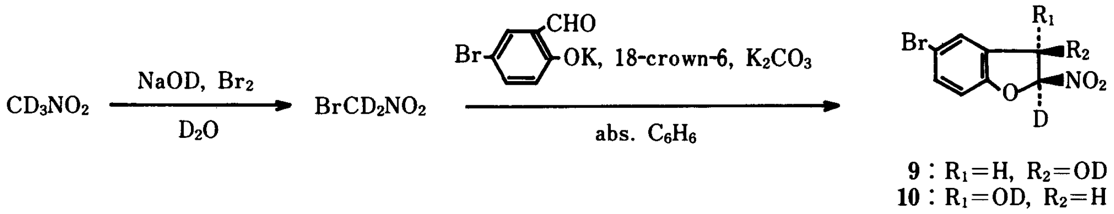

Chart 2

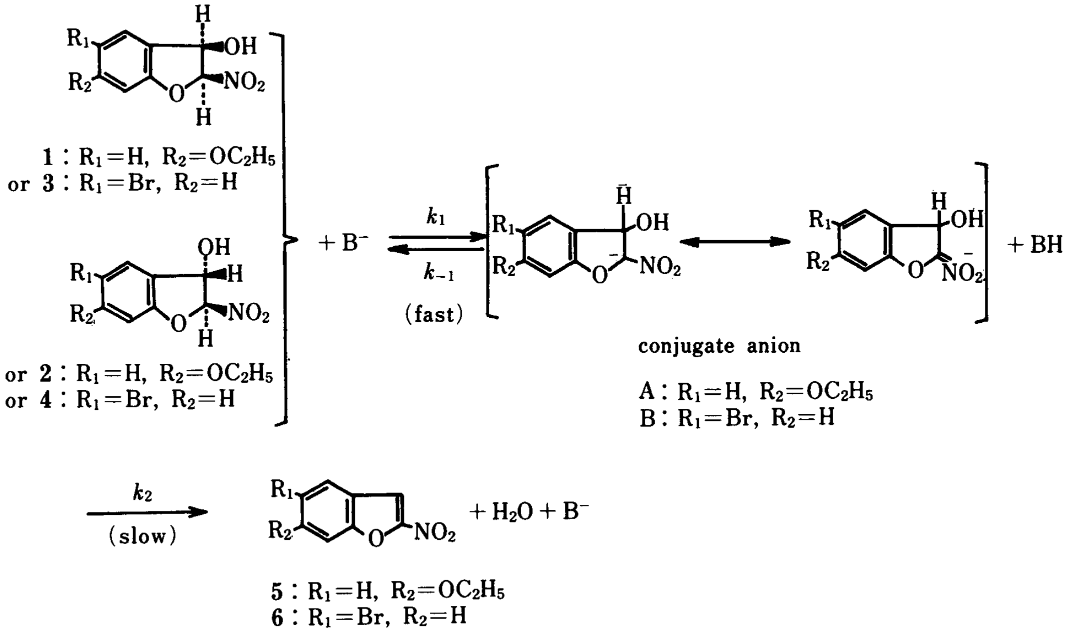

Chart 3

determined by the present procedure. Therefore, a clear leaving group effect was recognized and this indicated that the rate-determining step in the elimination of 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans is loss of the 3-hydroxy group from the conjugate anion, not deprotonation (Chart 3).[18]

Furthermore, kinetic studies using deuterium-labeled compounds (**9** and **10**) were carried out to examine the deuterium kinetic isotope effect. 5-Bromosalicylaldehyde potassium salt was treated with bromonitromethane-d_2 in absolute benzene in the presence of 18-crown-6 and dry K_2CO_3 to give a mixture consisting of **9** and **10**. The stereoisomers (**9** and **10**) could be separated from the isomeric mixture (Chart 2). The kinetic studies of the deuterium compounds (**9** and **10**) were performed under conditions similar to those used in the cases of **3** and **4** except for the use of KOD and C_2H_5OD instead of KOH and C_2H_5OH. The reaction rate constants (k_D) of **9** and **10** were $1.47 \times 10^{-2}\,\text{M}^{-1}\,\text{m}^{-1}$ and $1.67 \times 10^{-2}\,\text{M}^{-1}\,\text{m}^{-1}$, respectively. Consequently, the values of k_H/k_D were determined to be 1.3 and 1.2, respectively[19]; little deuterium isotope effect was observed. This indicated that the rate of deprotonation of the 3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans was significantly faster than the rate of loss of the 3-hydroxy group from the conjugate anions.

All the experimental results described above demonstrated that the elimination in the presence of an excess of KOH proceeded *via* the $(E1cB)_R$ mechanism (Chart 3).[13b,c,17d,g,20] Namely, *cis*- and *trans*-3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans (**1**, **2**, **3** and **4**) are instantaneously deprotonated and reversibly afford the carbanions at the 2-position in the presence of an excess of KOH. The carbanions can be stabilized as conjugate anions, and therefore there is no kinetic dependence on the diastereoisomerism of the substrates in the elimination. Subsequently, the elimination of the 3-hydroxy group from the conjugate anions results in production of 2-nitrobenzo[*b*]furans in the rate-determining step. Thus, we have identified here a new example of a typical $(E1cB)_R$ mechanism.[17a,d,21]

Experimental

All melting points were measured with a Thomas Hoover capillary melting point apparatus, and are uncorrected. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded with JEOL PS-100 spectrometer. Chemical shifts are given in ppm (δ) with tetramethylsilane (TMS) as an internal standard and the following abbreviations are used: s, singlet; d, doublet; dd, double doublet; br d, broad doublet. Low-resolution mass spectra (MS) were obtained with a Hitachi M-52 instrument, UV spectra with a Hitachi 124 spectrophotometer, and dual-wavelength UV spectra with a Hitachi 156 digital dual-wavelength spectrophotometer.

Dehydration of *cis*-5-Bromo-3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furan (3) to 5-Bromo-2-nitrobenzo[*b*]furan (6)——General Procedure for **1**, **2** and **4**: An ethanolic KOH solution (0.23 ml, containing 4.42 mg of KOH) was added to **3** (1.11 mg) in ethanol (50 ml) at 28.5 °C [concentration of **3**, 8.49×10^{-5} M; KOH, 1.57×10^{-3} M]. As soon as KOH was added to the ethanolic solution of **3**, the UV spectrum of the reaction mixture changed markedly to that of the carbanion intermediate (B). The UV spectrum of the mixture was recorded every 7 min over 1 h at 28.5 °C (Fig. 1); finally the carbanion (B) was converted to **6** in 92% yield, showing an isosbestic point at 284 nm. From **4** to **6**: yield 89%, isosbestic point 284 nm. From **1** to **5**, yield 93%, isosbestic point 300 nm. From **2** to **5**, yield 90%, isosbestic point 300 nm. (The yields were obtained on the basis of UV spectroscopy.)

Kinetic Studies of 3-Hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furans (1, 2, 3 and 4) *via* Carbanion Intermediate——General Procedure: An ethanolic solution (50 ml) of **3** (1.07 mg) or **4** (1.07 mg) was kept at 28.5 °C in a flask equipped with a soda lime tube. An ethanolic KOH solution (0.35 ml, containing 0.94 mg of KOH) was added to each solution (concentration of **3**, 8.15×10^{-5} M; **4**, 8.15×10^{-5} M; KOH, 3.32×10^{-4} M) and the decrease of absorbance ($\lambda_{269\,\text{nm}} - \lambda_{362\,\text{nm}}$)[14] of each solution was recorded every 5 min over 1 h at 28.5 °C by the use of the dual-wavelength UV spectrometer. During these reactions, the isosbestic point at 284 nm was checked every 10 min in the UV spectra of each solution. The reference cell contained an ethanolic KOH solution at the same concentration as used in the kinetic run. The kinetic data ($\lambda_{269\,\text{nm}} - \lambda_{362\,\text{nm}}$) showed excellent linearity (**3**, $r = 0.9982$; **4**, $r = 0.9980$). The rate constants of **3** and **4** were calculated to be $1.96 \times 10^{-2}\,\text{M}^{-1}\,\text{m}^{-1}$ and $1.99 \times 10^{-2}\,\text{M}^{-1}\,\text{m}^{-1}$, respectively, by the least-squares method from these kinetic data (run 3 in Table I). A similar procedure was used for the kinetic experiments on **1** and **2**. In the experiments on **1** and **2**, the decrease of absorbance ($\lambda_{266\,\text{nm}} - \lambda_{305\,\text{nm}}$) was recorded.[14] All results of the kinetic experiments are summarized in Table I.

Deuterium Incorporation and Isomerization of *trans*-5-Bromo-3-hydroxy-2-nitro-2,3-dihydrobenzo[*b*]furan (4)——A solution of KOD in C_2H_5OD (2 ml, containing 3.2 mg of KOD) was added to a solution of **4** (50 mg, 0.192 mmol) in C_2H_5OD (18 ml) at 28.5 °C. The UV spectrum of the mixture exhibited a strong absorbance ($\varepsilon \fallingdotseq 20000$) at 269 nm. After 2 min, 7.5 N DCl (0.04 ml) was added to the mixture. The UV spectrum of the mixture at this stage agreed with that of **4**. The mixture was concentrated under reduced pressure at 35 °C to give a pale yellow powder, which was identified as a mixture of *cis*- and *trans*-5-bromo-3-hydroxy[OD]-2-nitro-2,3-[2-D]dihydrobenzo[*b*]furan (**9** and **10**) (**9**:**10** $\fallingdotseq$ 1 : 3, deuterium incorporation 84%) by means of ^{1}H-NMR and mass spectrometry [*m/z*: 261 (M^+), 241, 215].

***cis*-3-Acetoxy-2-nitro-5-bromo-2,3-dihydrobenzo[*b*]furan (7)**——H_2SO_4 (95%, 0.05 ml) was added to a solution of **3** (350 mg, 1.35 mmol) in acetic anhydride (12 ml) at 25 °C. The solution was stirred at 25 °C for 5 min and poured into ice-water to give a colorless powder. The powder was collected by suction and recrystallized twice from CCl_4 to give **7** (colorless needles, 197 mg, 48%, mp 118—120 °C). *Anal.* Calcd for $C_{10}H_8BrNO_5$: C, 39.76; H, 2.67. Found: C, 39.88; H, 2.66. MS *m/z*: 301 (M^+), 255, 241, 213. IR $\nu_{\text{max}}^{\text{KBr}}\,\text{cm}^{-1}$: 2970, 1764, 1574, 1474, 1368. ^{1}H-NMR (acetone-d_6) δ: 1.96 (3H, s, CH_3), 6.42 (1H, d, 3-H), 6.66 (1H, d, 2-H), 6.82 (1H, d, 7-H), 7.26 (1H, s, 4-H), 7.28 (1H, d, 6-H). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ε): 288 (1785).

***trans*-3-Acetoxy-2-nitro-5-bromo-2,3-dihydrobenzo[*b*]furan (8)**——H_2SO_4 (95%, 0.1 ml) was added to a solution of **4** (800 mg, 3.08 mmol) in acetic anhydride (30 ml) at 25 °C. The solution was stirred for 10 min and poured into ice-water to give a colorless powder. The powder was recrystallized from CCl_4 to give **8** (colorless prisms, 470 mg, 51%, mp 97—99 °C). *Anal.* Calcd for $C_{10}H_8BrNO_5$: C, 39.76; H, 2.67. Found: C, 39.81; H, 2.63. MS *m/z*: 301 (M^+), 255, 241, 213. IR $\nu_{\text{max}}^{\text{KBr}}\,\text{cm}^{-1}$: 3030, 1763, 1580, 1472, 1370. ^{1}H-NMR (acetone-d_6) δ: 2.21 (3H, s, CH_3), 6.81 (1H, s, 3-H), 6.93 (1H, s, 2-H), 7.48 (1H, d, 6-H), 7.95 (1H, d, 7-H), 8.01 (1H, s, 4-H). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ε): 288 (2232).

Kinetic Studies of the Acetoxy Compound (7 and 8)——An ethanolic KOH solution (0.35 ml, containing 0.66 mg of KOH) was added to an ethanolic solution (50 ml) of **7** (1.29 mg) at 28.5 °C [concentration of **7**, 8.48×10^{-5} M; KOH, 2.34×10^{-4} M]. The mixture was kept at 28.5 °C and the UV spectrum was taken every 1.5 min.

However, the first UV spectrum was already superimposable on that of **6**, and it did not change at all later. The kinetic study of **8** was carried out by the same procedure as described above [concentration of **8**, 8.68×10^{-5} M; KOH, 2.84×10^{-4} M] and **8** was also converted to **6** within 1.5 min.

Bromonitromethane-d_2——Nitromethane-d_3 (25.7 g, 0.402 mol)[22] was added to a solution of NaOD (16.9 g, 0.423 mol) in D_2O (360 ml) at 5 °C. Bromine (69 g, 0.430 mol) was added in one portion to the mixture at 2 °C under vigorous stirring in a dry argon atmosphere. The solution was stirred for 1 h and extracted with dry ether. The ether layer was dried over Mg_2SO_4 and the solvent was evaporated off under reduced pressure to give pale yellow oily bromonitromethane-d_2 (54 g, 93%). IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1565, 1370, 1260, 746. ^{1}H-NMR: No signal was detected.

***cis*- and *trans*-5-Bromo-3-hydroxy[OD]-2-nitro-2,3-[2-D]dihydrobenzo[*b*]furan (9 and 10)**——Bromonitromethane-d_2 (5.0 g, 0.036 mol) was added to a mixture of dry 5-bromosalicylaldehyde potassium salt (7.2 g, 0.030 mol), 18-crown-6 (0.8 g, 0.003 mol) and dry K_2CO_3 (4.1 g, 0.036 mol) in absolute benzene (300 ml) at 21—23 °C for 15 min in a dry argon atmosphere. The mixture was stirred at 25 °C for 30 min and then filtered. The filtrate was concentrated under reduced pressure to give a pale yellow oil. The oil was treated with dry CCl_4 to give a colorless powder (3.7 g). Upon recrystallization from dry CCl_4, the *trans* isomer (**10**) crystallized first as colorless prisms (1.9 g, 24%). mp 103—104 °C. MS *m/z*: 261 (M^+), 241, 215, 136. ^{1}H-NMR (acetone-d_6) δ: 5.30 (1H, s, 3-H), 6.11 (trace, s, 2-H), 7.34 (1H, d, 7-H), 7.80 (1H, dd, 6-H), 7.88 (1H, d, 4-H). Concentration and cooling of the mother liquor yielded the crude *cis* isomer (**9**), which was purified by several fractional crystallizations from dry $CHCl_3$ and CCl_4 to give colorless fine needles (0.23 g, 3%). mp 147—148 °C. MS *m/z*: 261 (M^+), 241, 215, 136. ^{1}H-NMR (acetone-d_6) δ: 5.74 (1H, br d, 3-H), 6.22 (trace, br d, 2-H), 7.47 (1H, d, 7-H), 7.98 (1H, dd, 6-H), 8.00 (1H, d, 4-H). **9** and **10** were contaminated with about 4% of **3** and **4**, respectively, on the basis of ^{1}H-NMR spectral data.

Kinetic Deuterium Isotope Effect——Solutions of **9** and **10** in C_2H_5OD (35 ml, containing 0.76 mg of **9** or 0.75 mg of **10**) were placed in a flask equipped with a soda lime tube at 28.5 °C. A solution of KOD in C_2H_5OD (0.07 ml, containing 1.3 mg of KOD) was added to each solution at 28.5 °C (concentration of **9**, 1.09×10^{-4} M; **10**, 1.08×10^{-4} M; KOD, 6.50×10^{-4} M). The rate constant of each reaction mixture was determined by the same procedure as used in the cases of the kinetic experiments on **3** and **4**. The obtained rate constants were 1.47×10^{-2} M^{-1} m^{-1} in the case of **9** and 1.67×10^{-2} M^{-1} m^{-1} in the case of **10**. Consequently, the values of kinetic deuterium isotope effect (k_H/k_D) were 1.3 ($1.96 \times 10^{-2}/1.47 \times 10^{-2}$) for **3** and 1.2 ($1.99 \times 10^{-2}/1.67 \times 10^{-2}$) for **4**.[19]

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12) The diastereoisomers (**1** and **2**) showed similar UV spectra, and the UV spectra of **3** and **4** were also nearly the same as each other [UV $\lambda_{\max}^{\text{EtOH}}$ nm (ε): **1**, 283 (3429); **2**, 283 (3469); **3**, 286 (2076); **4**, 286 (2087)].

13) Stable carbanions can be obtained from naphthalene, anthracene, biphenyl and some other compounds. To elucidate the structures of the carbanions their electronic absorption spectra were studied [*a*) G. Hafelinger and A. Streitwieser, Jr., *Chem. Ber.*, **101**, 657 (1968); *idem, ibid.*, **101**, 672 (1968); [*Chem. Abstr.*, **53**, 21798*b* (1959)]; I. V. Astaf'ev and A. I. Shateshtein, *Optika Spektroskopiya*, **6**, 631 (1959); E. De Boer, "Advance in Organometallic Chemistry," Vol. 2, Academic Press, New York, 1964, p. 115]. Carbanions (nitronate ions) of 2-phenyl-2-acetoxy-1-nitrocyclohexanes or 2-phenyl-2-methoxy-1-nitrocyclopentanes were also detected [*b*) F. G. Bordwell, K. C. Yee and A. C. Knipe, *J. Am. Chem. Soc.*, **92**, 5945 (1970); *c*) F. G. Bordwell, M. M. Vestling and K. C. Yee, *ibid.*, **92**, 5950 (1970)].

14) Compound **5** has equal absorbance at 266 and 305 nm. Thus, the decrease of absorbance ($\lambda_{266\,\text{nm}} - \lambda_{305\,\text{nm}}$) shows

the consumption of the conjugate anion (A). Similarly, the decrease of absorbance ($\lambda_{269\,\mathrm{nm}} - \lambda_{362\,\mathrm{nm}}$) indicates that of B.

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19) The rate constants (k_H) of **3** and **4** were $1.96 \times 10^{-2}\,\mathrm{M}^{-1}\,\mathrm{m}^{-1}$ and $1.99 \times 10^{-2}\,\mathrm{M}^{-2}\,\mathrm{m}^{-1}$ respectively (Table I).
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22) Nitromethane-d_3 was purchased from the Commissariat á L'Energie Atomique, France.