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The Confirmation of the Configuration of Ethyl 2-Bromo-3-nitro-2-alkenoate by ^{13}C NMR Spectroscopy

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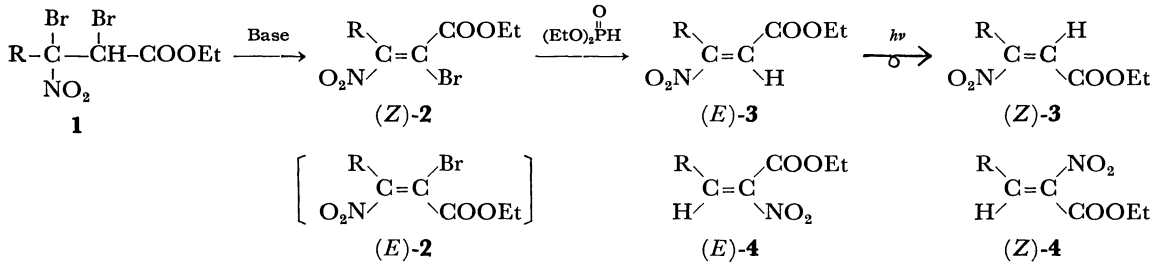
The configuration of the ethyl 2-bromo-3-nitro-2-alkenoate formed by the elimination of hydrogen bromide from ethyl 2,3-dibromo-3-nitroalkanoate was determined to be (*Z*) by the examination of the ^{13}C NMR spectra.

In a previous paper, it was found that the base-catalyzed elimination of hydrogen bromide from a *threo* and *erythro* mixture of ethyl 2,3-dibromo-3-nitroalkanoate (**1**) afforded only one kind of geometric isomer of ethyl 2-bromo-3-nitro-2-alkenoate (**2**).[1] The same phenomenon was also observed in the case of a *threo* and *erythro* mixture of ethyl 2-acetoxy-3-nitroalkanoate.[2] The configuration of **2** was deduced to be (*Z*) from the fact that the reduction of **2** with diethyl phosphonate gave ethyl 3-nitro-2-alkenoate (**3**) with the (*E*)-configuration,[3] the geometry of which was determined by ^{1}H NMR spectroscopy.[1]

In the present investigation, the authors measured the ^{13}C NMR spectra of **2** and related compounds in order to confirm the configuration of **2** and then discussed the reaction mechanism.

Results and Discussion

The ^{13}C NMR chemical shifts of Compounds **2** and **3** and of ethyl (*E*)- and (*Z*)-2-nitro-2-alkenoates [(*E*)-**4**, and (*Z*)-**4**] are presented in Table 1. It is noticeable that, in every (*E*), and (*Z*) isomeric pair of 3-nitro-2-alkanoate, **3**, each carbon at positions C-1, C-2, and C-3 (for numbering, see Table 1) of the (*Z*)-isomer always resonates at a higher field than does the corre-



1 (*Z*)-**2** (*E*)-**3** (*Z*)-**3**

(*E*)-**2** (*E*)-**4** (*Z*)-**4**

Scheme 1.

Table 1. ^{13}C chemical shifts of carbons[a] in **2**, **3**, and **4**

Compound	R		C-2′ δ/ppm	C-1′ δ/ppm	C-1 δ/ppm	C-2 δ/ppm	C-3 δ/ppm	C-4 δ/ppm	C-5 δ/ppm	C-6 δ/ppm
2	Et		13.6	63.5	161.7	118.9	155.9	25.9	10.6	
	n-Pr		13.7	63.5	161.8	119.6	155.0	33.9	20.1	13.4
	i-Pr		13.7	63.6	162.2	113.5	160.4	32.9	18.7	
3	Me	(*Z*)	14.0	61.9	163.0	116.7	155.9	18.9		
		(*E*)	14.0	62.0	164.4	121.5	160.4	14.2		
	Et	(*Z*)	14.1	61.9	162.8	113.9	162.4	26.8	11.0	
		(*E*)	14.2	61.9	165.6	120.9	164.1	21.4	12.5	
	i-Pr	(*Z*)	14.0	61.6	166.7	111.8	162.4	32.5	19.2 19.9	
		(*E*)	14.2	61.8	169.4	118.9	164.1	28.2	19.7	
	n-Pr	(*Z*)	13.9	61.6	162.3	114.5	160.4	34.9	20.0	13.0
		(*E*)	14.3	62.0	164.3	121.4	164.3	29.4	21.8	13.8
4	Me	(*Z*)	14.1	63.0	159.0	146.1	136.1	13.5		
		(*E*)	14.1	62.9	160.1	146.1	140.0	13.5		
	Et	(*Z*)	14.1	62.9	159.3	145.0	141.5	21.9	12.3	
		(*E*)	14.1	62.8	160.1	145.0	141.5	21.8	12.5	
	n-Pr	(*Z*)	14.1	62.9	158.9	145.3	139.8	30.2	21.5	13.7
		(*E*)	14.1	62.7	160.1	145.3	143.3	30.0	21.8	13.7

a) The carbons were commonly numbered as follows: $\overset{6}{C}-\overset{5}{C}-\overset{4}{C}-\overset{3}{C}X=\overset{2}{C}Y-\overset{1}{C}OO\overset{1'}{C}H_2\overset{2'}{C}H_3$.

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sponding carbon of the (*E*)-isomer. This tendency is, however, less pronounced in the case of 2-nitro-2-alkenoate, **4**.

Savitsky *et al.*[4] reported that the chemical shift of olefinic carbons of 3-substituted alkenoate with two bulky substituents in a *cis* orientation deviates from the expected value due to the alteration in the electron density by the steric inhibition of the resonance. Consequently, the above facts are attributed to the diminished electron-withdrawing effect of the nitro and ethoxycarbonyl groups of (*Z*)-**3** in the *cis* orientation. This empirical fact is a useful clue for the determination of the configuration of the isomeric pair of **2**; however, it is not applicable when only one isomer is available, as in the present case. Therefore, the observed ^{13}C shifts of olefinic carbons in **2** were compared with those calculated from the results of (*E*)- and (*Z*)-**3** and the substituent effect. The substituent effects for a series of 2-alkenoates have been studied by Lippmaa *et al.*[5,6] and by Brower and Stothers,[7] and the substituent parameter of the bromine atom suggested by Lippmaa *et al.* was used for the calculation here; that is, the shifts of the C-2 and C-3 of **3** were corrected by 8.0 ppm to an upper field by the bromination of C-2. The results are presented in Table 2. The observed shifts agree well with the calculated values for the (*Z*)-isomer, but not with those of the (*E*)-isomer. This is in accordance with our previous deduction.[1] However, it should be noticed that the observed shifts of the C-2 of (*Z*)-**2** deviate comparatively much from the calculated shifts. This deviation might also be attributed to the *cis* configuration between the bromine atom and the nitro group in (*Z*)-**2**, because such crowded compounds were not used by Lippmaa *et al.*[5,6] in determining the substituent parameters.

TABLE 2. CALCULATED AND OBSERVED ^{13}C CHEMICAL SHIFTS OF THE OLEFINIC CARBONS OF **2**

R	Calcd and obsd		^{13}C shifts (δ/ppm) C-2	C-3
Et	Calcd	(*Z*)	112.9	156.1
		(*E*)	105.9	154.4
	Obsd		118.9	155.9
i-Pr	Calcd	(*Z*)	110.9	156.1
		(*E*)	103.8	154.4
	Obsd		113.5	160.4
n-Pr	Calcd	(*Z*)	113.4	156.3
		(*E*)	106.5	152.4
	Obsd		119.6	155.0

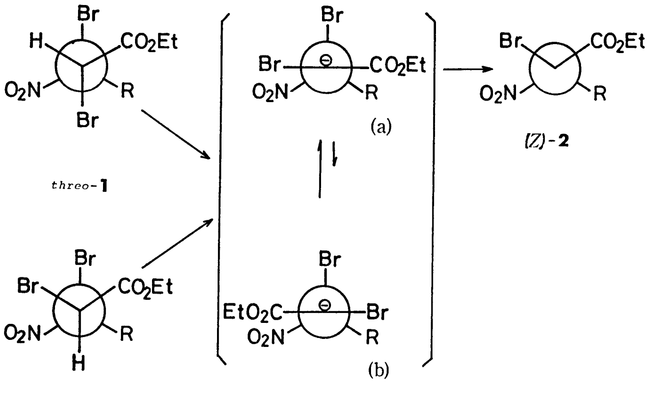
TABLE 3. THE SUBSTITUENT SHIFT[a] OF C-2 AND C-3 CAUSED BY THE NITRO GROUP ON THE C-3 OF **3** AND ON THE C-2 OF **4**

Compound	R	(*Z*) C-3	(*Z*) C-2	(*E*) C-3	(*E*) C-2
3	Me	14.2	0.5	9.9	−6.1
	Et	8.9	1.2	8.7	−6.8
	i-Pr	4.6	1.3	4.2	−7.1
	n-Pr	11.2	1.5	8.2	−7.0
4	Me	−10.1	25.1	−9.9	23.3
	Et	−13.7	25.3	−12.2	24.3
	n-Pr	−9.8	25.4	−12.4	23.8

a) The differences in chemical shifts between **3** or **4** and the correspondlng 2-alkenoates are shown in δ/ppm. Consequently, the negative sign implies a higher field shift upon substitution with a nitro group.

An analogous tendency is found in the differences in the chemical shifts (*Δδ*/ppm) of the olefinic carbons of **3** or **4** and the corresponding 2-alkenoates with no nitro group[7] (Table 3). In the case of **4** with a nitro group on C-2 both (*Z*)- and (*E*)-isomers showed a similar trend. That is, the substituent shifts for both isomers were 23—25 ppm lower for C-2, to which a nitro group is attached, and 10—13 ppm higher for C-3. On the other hand, in the case of **3**, where the nitro group is attached to C-3, the substituent shifts exhibited quite different profiles. For the (*E*)-isomer, C-2 showed field shifts higher by 6—7 ppm and C-3 field shifts lower by 4—10 ppm, as was observed in the case of **4**. In contrast, the C-2 and C-3 of the (*Z*)-isomer shifted to fields lower by 0.5—1.5 and 4—14 ppm respectively. These anomalous shifts may be attributed to the factor mentioned above.

In conclusion, it can be said that the substitution shifts are strongly affected by the configuration and the position of the substituent. If the stereoelectronic influence is taken into account in the estimation of the substituent shift of the bromine atom, a much better consistency will result than is found in Table 2.



Scheme 2.

The above results show that both the *erythro* and *threo* isomers of **1** afforded only the (*Z*)-isomer of **2**. It means that the elimination from the two isomers proceeds *via* a common intermediate, analogous to the *E1cB* mechanisms proposed by Cummings and Kreuz[8] and by Kaplan *et al.*[9,10] As is shown in Scheme 2, the deprotonation of both diastereomers of **1** will result in the formation of a common, resonance-stabilized carbanion. Although two conformations, in which the leaving bromine atom is in a proper disposition for elimination, are possible for this anion, (a) will predominate over (b) because of the electrostatic repulsion between nitro and ethoxycarbonyl groups. Thus, the predominant formation of (*Z*)-**2** will result.

Experimental

The ^{13}C NMR spectra were recorded at 30 °C on a JEOL

JNM FX-100 spectrometer in the pulse Fourier transform mode at 25.15 MHz. Each spectrum was obtained after 1000 transients with a frequency range of 6250 Hz. The pulse angle of 45° was used, with an acquisition time of 0.8 s and a pulse delay of 0.7 s. All the measurements were carried out in a deuteriochloroform solution containing a drop of TMS as the internal standard. The chemical shifts were recorded in δ/ppm.

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