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The ^{1}H NMR Spectral Detection and Kinetic Analysis of the Conformational Change of 4,4,5,5- and 6,6,7,7-Tetramethoxycycloheptadienones

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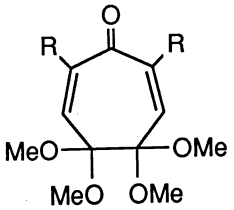
The variable temperature ^{1}H NMR measurements of 4,4,5,5- and 6,6,7,7-tetramethoxycycloheptadienones disclosed an existence of the bond-twisting conformers. The complete line shape analysis by the simulation method gave the activation parameters of the interconversion barrier.

When we prepared o- and p-tropoquinone bisacetals by means of an anodic oxidation of dimethoxytropones,[1,2] we noticed that their ^{1}H and ^{13}C NMR spectra showed a considerable broadening of the MeO signals of bisacetals derived from 2,3- and 4,5-dimethoxytropones even at 20 °C due to a dynamic process. Recently, Weissensteiner et al. made a conformational analysis of 10,11-dihydrodibenzo[a,d]cyclohepten-5-one by means of X-ray diffraction and NMR spectroscopic studies.[3] Herein, we describe the kinetic aspects of the interconversion of our monocyclic tetramethoxycycloheptadienones.

The ^{1}H NMR of 4,4,5,5-tetramethoxycyclohepta-2,6-dienones (**1**) at 25 °C showed two broad MeO signals, while that of 6,6,7,7-tetramethoxycyclohepta-2,4-dienone (**2**) showed a sharp signal for two MeO and a broad signal for two MeO. Variable temperature measurement of the ^{1}H NMR of **1** (between -60 °C and 60 °C) and complete line shape analysis by the simulation method[4] provided kinetic parameters listed in Table 1.

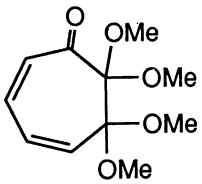


a R = H

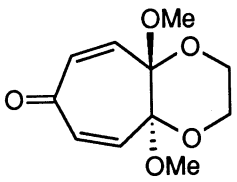
b R = Me

c R = Pr

1



2



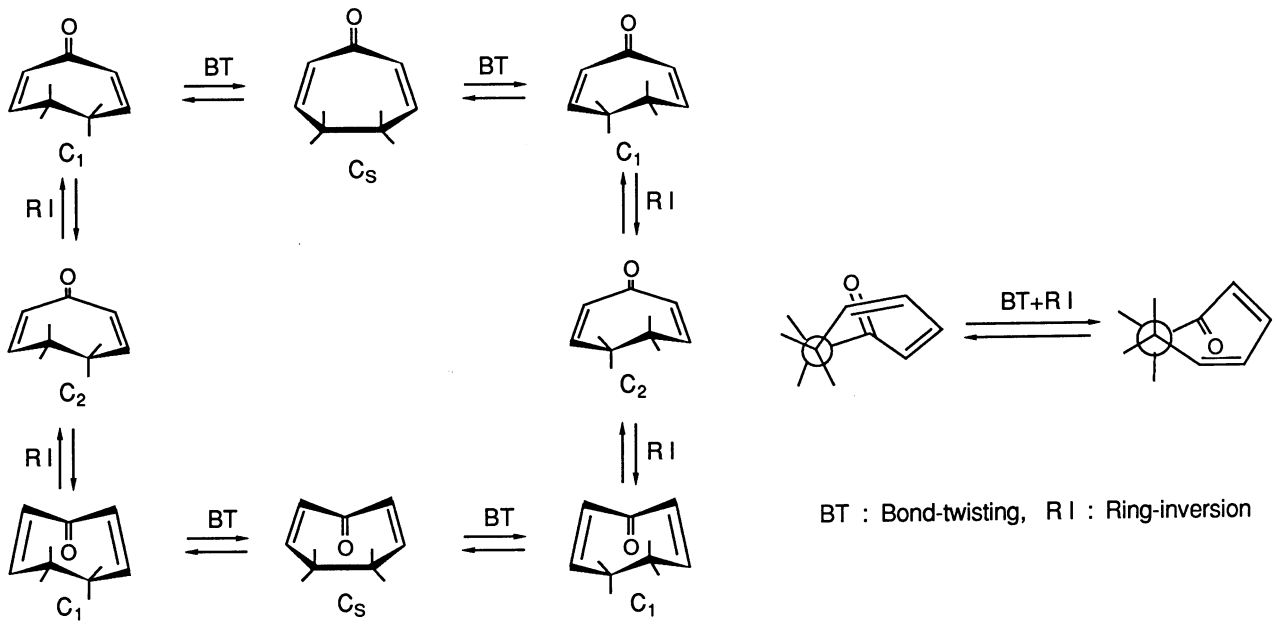
3

There are two molecular motions in the system of **1**;[3] i.e., the flipping of the carbonyl group (ring inversion) of the cycloheptadienone via a C_2 symmetrical transition state and the bond-twisting at the sp^3-carbons to exchange between two half-boat forms (bond-twisting) via a C_s symmetrical transition state. 4,5-Ethylenedioxy-4,5-dimethoxycyclohepta-2,6-dienone (**3**)[5] showed no broadening of

the MeO signal even at -60 °C, confirming the rapid ring inversion. Since two MeO signals of **1** appeared separately at -60 °C, the cycloheptadienone is operating a rapid ring inversion but no twisting of the C-C bond. On the other hand, **2** behaved differently; the ^{1}H NMR of **2** at -30 °C showed four MeO signals, indicating a frozen molecular motion. An appearance of four MeO signals in **2** can be explained in terms of fixed twisted-boat conformer. The ring inversion and the bond twisting operated simultaneously in **2**. All $\Delta H^{\neq}$ values of **1**, ca. 56 kJ mol^{-1}, were larger than that of **2**, and no substituent effect of the dialkyl groups on the C-2 and C-7 was observed.

Table 1. Activation parameters for the interconversion

	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta G^{\neq}$/kJ mol^{-1} at 298 K	r
1a	56.5±1.3	-20.5±4.2	62.7±2.5	0.9996
1b	59.0±2.9	-18.8±9.2	64.8±5.9	0.9985
1c	56.9±1.3	-25.5±3.3	64.4±2.1	0.9998
2	42.6±2.5	-45.6±10.0	56.4±5.9	0.9956



A more rapid conformational change of **2** is explained in that the ring inversion can make the bond twisting easy because two exchanging parts are directly connected. The larger value of $\Delta S^{\neq}$ is probably due to that the exchanging part in **2** is wider than that in **1**.

References

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3) W. Weissensteiner, O. Hofer, and U. G. Wagner, J. Org. Chem., 53, 3988 (1988).
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