

**(E-Z) ISOMERIZATION of  $\alpha,\beta$ -UNSATURATED KETONES**

Tomáš VONDRÁK and Miloš PROCHÁZKA

*Department of Organic Chemistry,  
Charles University, 128 40 Prague 2*

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Thermodynamic parameters have been determined for the (*E-Z*) equilibria of title ketones  $X-CH=CH-CO-CH_3$  ( $X = Cl, CH_3, OCH_3$ ); the energy difference of the isomers calculated by the MO CNDO/2 method for the optimum conformations is lower than  $\Delta H$  by 7–8 kJ mol<sup>-1</sup>.

So far only few data are available on *E-Z* equilibria of unsaturated ketones. The following  $K(Z/E)$  values were found for the prototropic isomerizations:  $9.7 \cdot 10^{-3}$  (3-penten-2-one at 308 K) (ref.<sup>1</sup>) and  $41 \cdot 10^{-3}$  (4-hexen-3-one<sup>2</sup> at 318 K). As the (*E-Z*) equilibria of halogenolefins and alkoxyolefins are known to be shifted in favour<sup>3-7</sup> of the (*Z*)-isomers, we followed these equilibria in a series of ketones  $X-CH=CH-COCH_3$  for  $X = CH_3, Cl,$  and  $OCH_3$ . The equilibrium of alkoxyolefins is known to be shifted in favour of the (*Z*)-isomer with increasing branching of the alkyl group, which is explained<sup>3,4</sup> on the basis of conformation equilibria. Epiotis and coworkers<sup>8,9</sup> consider the shift of the equilibrium of alkoxyolefins in favour of the (*Z*)-isomers to be due to interaction of *p* orbital of the heteroatom with  $\pi$ -type orbitals connected with charge transfer to antibonding olefinic orbital.

Table I gives results of the isomerizations; except for 4-chloro-3-buten-2-one, the isomerizations were catalyzed with mercury(II) acetate which did not cause any side reactions at the temperatures given. The isomerization of 4-chloro-3-buten-2-one was induced thermally without catalyst, because mercury(II) acetate caused decomposition. The (*E*)-isomers are predominant in the equilibria, the amounts of (*Z*)-isomers increase in the series  $CH_3O < CH_3 < Cl$ , in the same order are decreasing both the  $\Delta H$  and  $\Delta S$  terms, the former being decisive. Energy of the isomers was calculated by the CNDO/2 method<sup>10</sup> with *sp* basis (for chlorine *spd* basis, too) using parametrization by Santry-Segal<sup>11</sup>. The quantum-chemical calculations were carried out with geometry parameters of cognate molecules found experimentally. Syn-periplanar position of hydrogen atom and C=O bond was chosen for  $CH_3C=O$  group<sup>12</sup>; moreover, energy differences of rotation isomers were calculated, and the obtained optimum conformations were compared with those derived from spectral data.

In the case of 4-chloro-3-buten-2-one, bond energies were calculated in dependence on torsion angle between C=C and C=O bonds using both *sp* and *spd* bases

(Fig. 1). The *sp* basis gives, for the both isomers, the synclinal conformation as the lowest in energy, the torsion angles being  $40 \pm 5^\circ$  and  $80 \pm 5^\circ$  for the (*E*)- and (*Z*)-isomers, respectively; however, the two conformations differ from synperiplanar conformation by  $3-5 \text{ kJ mol}^{-1}$  only. The *spd* basis gives synclinal conformation as the optimum for the (*E*)-isomer (torsion angle  $70 \pm 5^\circ$ ), whereas antiperiplanar conformation with strong *d*-orbital bonding interaction between chlorine and hydrogen ( $\text{Cl}\cdots\text{H}_3\text{C}$ ) is the optimum for the (*Z*)-isomer. Benson and Pohland<sup>13</sup> ascribe antiperiplanar  $\text{C}=\text{C}-\text{C}=\text{O}$  conformation to the (*E*)-isomer on the basis of IR spectra, Dabrowski and Terpinsky<sup>14</sup> ascribe to this isomer two stable conformations (synperiplanar and anticlinal) of comparable energies (on the basis of IR spectra, too). Our MO CNDO/2 calculations agree with the interpretations of ref.<sup>14</sup>. To compare the bond energies, we took synperiplanar conformation of  $\text{C}=\text{C}-\text{C}=\text{O}$  (Eq. (1)) and obtained (in *sp* basis) an energy difference of  $5.5 \text{ kJ mol}^{-1}$  in favour of the (*E*)-isomer and (in *spd* basis) an energy difference of  $5.7 \text{ kJ mol}^{-1}$  in favour of the (*Z*)-isomer, which disagrees with reality. Using the approximation of constant bond lengths, we calculated for (*E*)- and (*Z*)-3-penten-2-ones the energy corresponding to rotation of  $\text{C}_{(1)}\text{H}_3$  group at the angles  $0^\circ$  (*sp* position of  $\text{C}-\text{H}$  and  $\text{C}=\text{C}$  bonds),  $30^\circ$ , and  $60^\circ$  (*sc*), the  $\text{C}=\text{C}-\text{C}=\text{O}$  segment being in synperiplanar position. The found most favourable conformation of the (*E*)-isomer was synperiplanar with a rotation barrier of  $5.5 \text{ kJ mol}^{-1}$ , that of the (*Z*)-isomer was synclinal with angle  $60^\circ$  and a rotation barrier of  $11 \text{ kJ mol}^{-1}$ , the *sp* confirmation being at the top of the barrier (Eq. (2)). The dependence of bond energy on torsion angle of  $\text{C}=\text{C}-\text{C}=\text{O}$  bonds indicates a possibility of non-planar conformations of the (*E*)-isomer with a torsion angle  $40^\circ$  and with flat energy minimum and small energy difference ( $0.8 \text{ kJ mol}^{-1}$ ) from the synperiplanar conformation. From IR spectra it was derived<sup>15</sup> that the synperiplanar and antiperiplanar conformations are present at the ratio 0.45. Forster and coworkers<sup>16</sup> analyzed microwave spectrum of the cognate 3-buten-2-one and found its antiperiplanar conformation to be the most favourable. If synperiplanar

TABLE I  
Equilibrium data of the *E-Z* isomerizations

$E \rightleftharpoons Z$	Range of measurement, K	$\Delta G_{298}$ $\text{kJ mol}^{-1}$	$\Delta H$ $\text{kJ mol}^{-1}$	$\Delta S$ $\text{J mol}^{-1} \text{K}^{-1}$
4-Methoxy-3-buten-2-one	326-423	12.2	14.4	7.4
3-Penten-2-one	326-469	11.3	12.9	5.7
4-Chloro-3-buten-2-one	343-393	10.7	11.8	3.7

position was chosen between  $C_{(1)}-H$  and  $C=C$  bonds, then the found optimum  $C=C-C=O$  conformation was synclinal with torsion angle  $80 \pm 5^\circ$ , the energy difference between this conformation and the synperiplanar one being  $11.6 \text{ kJ mol}^{-1}$ . If synclinal position was chosen between  $C_{(1)}-H$  and  $C=C$  bonds, then the found optimum  $C=C-C=O$  conformation was synperiplanar (Eq. (3)). According to interpretation of IR spectra<sup>17,18</sup>, synperiplanar conformation of  $C=C-C=O$  bonds is assigned to (*Z*)-3-penten-2-one. For comparison of bond energies of the isomers we used synperiplanar conformations of the  $H-C-C=O$  and  $C=C-C=O$  bonds, the calculated energy difference was  $5 \text{ kJ mol}^{-1}$  in favour of the (*E*)-isomer (Table II).

Bond energy changes of  $CH_3O$  group conformations of (*E*)- and (*Z*)-4-methoxy-3-buten-2-ones are given in Fig. 2 for more advantageous synperiplanar positions of  $C=C$  and  $C=O$  bonds. For the (*E*)-isomer two favourable conformations of  $CH_3O$

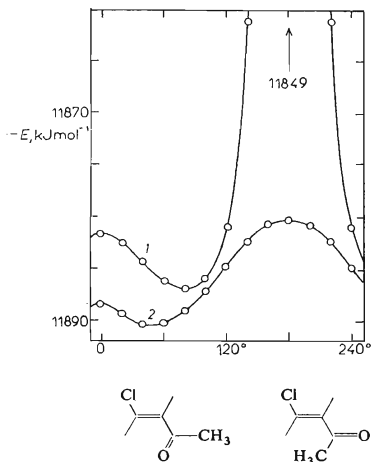


FIG. 1

Dependence of the calculated bond energy (*sp* basis) of 4-chloro-3-buten-2-one on conformation of  $C=C-C=O$  segment Curve 1 (*Z*)-isomer, 2 (*E*)-isomer

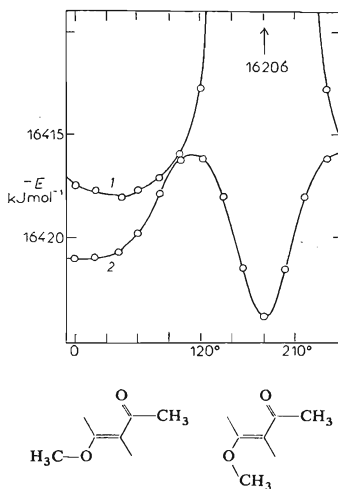


FIG. 2

Dependence of the calculated bond energies of (*Z*)- (curve 1) and (*E*)-4-methoxy-3-buten-2-one (curve 2) on conformation of  $H_3CO-C=C-C=O$  segment (*sp* conformation of  $C=C-C=O$  segment)

group were calculated, synperiplanar and antiperiplanar, the former being preferred by  $2.5 \text{ kJ mol}^{-1}$ . These calculated conformations agree with interpretation of IR spectra<sup>19</sup>. For the  $(Z)$ -isomer with  $sp$  position of  $\text{C}=\text{C}-\text{C}=\text{O}$  bonds the found optimum conformation was anticlinal with torsion angle  $140 \pm 5^\circ$ , but the energy difference between this optimum  $ac$  conformation and  $ap$  is negligible ( $0.5 \text{ kJ mol}^{-1}$ ). The bond energy difference between the two isomers in synperiplanar conformations of  $\text{C}=\text{C}-\text{C}=\text{O}$  bonds (which was calculated to be more favourable than  $ap$  conformation for the both isomers) is  $5.7 \text{ kJ mol}^{-1}$  in favour of the  $(E)$ -isomer, if the optimum conformations of  $\text{CH}_3\text{O}$  groups are used. The  $\text{CH}_3\text{O}$  group of the  $(E)$ -isomer can assume the  $sp$  conformation which is excluded in the  $(Z)$ -isomer, and this fact contributes to higher thermodynamic stability of the  $(E)$ -isomer. This interpretation agrees with proposals of Taskinen and Liukas<sup>3</sup>. For  $(E)$ -1-methoxypropene we calculated<sup>20</sup> two favourable conformations of approximately the same energy, synperiplanar and anticlinal with torsion angle  $50^\circ$ . The stability degree of  $sp$  conformation of  $\text{CH}_3\text{O}$  group in  $(E)$ -4-methoxy-3-buten-2-one (as compared

TABLE II

The bond energy differences ( $\text{kJ mol}^{-1}$ ) calculated by MO CNDO/2 ( $sp$  basis, synperiplanar conformation of  $\text{C}=\text{C}-\text{C}=\text{O}$ )

Isomer	Mono-centric part	Bicentric	Total
4-Chloro-3-buten-2-one			
$Z$	3 773.4	-15 655.2	-11 881.7
$E$	3 774.5	-15 661.8	-11 887.2
Difference	-1.1	6.6	5.5
4-Methoxy-3-buten-2-one			
$Z$	5 139.6	-21 557.2	-16 417.4
$E$	5 140.7	-21 561.6	-16 420.9
Difference	-0.9	4.4	3.5
3-Penten-2-one			
$Z$	4 515.0	-20 010.0	-15 495.0
$E$	4 504.6	-20 004.6	-15 500.0
Difference	10.4	-5.4	5.0

with 1-methoxypropene) is affected by a more extensive conjugation of  $p_z$  AO of oxygen with  $\pi$  orbital of C=C bond. In 1-methoxypropene this conjugation is small and its energy contribution is overbalanced by repulsion of the other atoms, which results in equalization of energies of  $ac$  and  $sp$  conformations. Carbonyl group in methoxybutenone molecule increases  $O_{pz}-\pi$  conjugation, and this energy contribution exceeds the repulsion  $-\text{OH}_3\text{C}\cdots\text{H}-\text{C}=\text{C}$ . The  $\pi$  bond order of  $\text{CH}_3\text{O}-\text{C}$  bond of (*E*)-isomers of 4-methoxy-3-buten-2-one was calculated 0.31, that of 1-methoxypropene 0.26 with simultaneous increase of charge at the oxygen atom. In all, the equilibrium of the two isomers is affected predominantly by antibonding interactions in the (*Z*)-isomer.

Comparison of the calculated energy differences and experimental values (Table III) indicates that, the overall predominance of the (*E*)-isomers in the equilibria being correctly calculated, the  $\Delta E$  value are distinctly lower than  $\Delta H$  values and are little differing in the series  $\text{CH}_3\text{O}$ ,  $\text{Cl}$ ,  $\text{CH}_3$ . The results can be unfavourably affected by using equal values of distances and angles for the two isomers. Experimental data are not known. A part of the energy effects causing the high relative predominance of (*E*)-4-methoxy-3-buten-2-one must be ascribed to the fact that  $\text{CH}_3\text{O}$  group can assume the synperiplanar conformation which is excluded for sterical reasons in the (*Z*)-isomer. Application of  $d$  orbitals in calculations of the chloro derivatives gives no good results and needs a modification of parameters.

### EXPERIMENTAL

Purity of the compounds was checked by gas chromatography. The  $^1\text{H}$  NMR spectra were measured with a Tesla 80 MHz spectrometer using hexamethyldisiloxane as internal standard,  $\delta$  scale,  $\text{CCl}_4$ . The mass spectra in connection with GC were measured with a JEOL D 100 apparatus (Japan).

TABLE III

Comparison of experimental  $\Delta H$  values with calculated  $\Delta E$  differences for isomeric  $\text{X}-\text{CH}=\text{CH}-\text{CO}-\text{CH}_3$  ( $\text{kJ mol}^{-1}$ )

X	$\Delta E$	$\Delta H - \Delta E$
Cl	5.5 <sup>a</sup> -5.7 <sup>b</sup>	6.3 17.5
$\text{CH}_3$	5.0	7.9
$\text{OCH}_3$	5.7 <sup>c</sup> 3.5 <sup>d</sup>	8.7 10.9

<sup>a</sup>  $sp$  Basis; <sup>b</sup>  $spd$  basis; <sup>c</sup> the most favourable conformation of  $\text{CH}_3\text{O}$  group; <sup>d</sup>  $ap$  conformation of  $\text{CH}_3\text{O}$  group.

## Preparation of Compounds

(*E*)- and (*Z*)-3-penten-2-ones were prepared according to ref.<sup>1</sup>, the isomers were purified by preparative GC (Chromaton N-AW-DMCS 0.20 mm with 10% silicone elastomer XE 60). The (*E*)-isomer was obtained in the purity of 99.5%, b.p. 122°C/100 kPa, the (*Z*)-isomer of 98% purity, b.p. 111°C/100.1 kPa.

(*E*)-4-Methoxy-3-buten-2-one was prepared according to ref.<sup>21</sup>, the mixture with approximate *E/Z* ratio 98 : 2 was separated on a column of 40 TP. The (*E*)-isomer was isolated in 99.6% purity, b.p. 69°C/2 kPa. <sup>1</sup>H NMR spectrum: 2.13 s CH<sub>3</sub>-C; 3.64 s C(H)<sub>3</sub>O; 5.44 d, 7.42 dH-C=, I = 13.2 Hz. The (*Z*)-isomer could not be isolated.

A 98 : 2 mixture of (*E*)- and (*Z*)-4-chloro-3-buten-2-ones (b.p. 30–32.5°C/2.4 kPa) was prepared by addition of acetyl chloride to ethine catalyzed with aluminium chloride<sup>22</sup>; the mixture was distilled on a column to give the (*E*)-isomer of 99.0% purity, b.p. 32.5°C/2.4 kPa. <sup>1</sup>H NMR spectrum: 2.20 CH<sub>3</sub>C; 6.43 d, 7.32 d H-C=, J = 13.8 Hz. The (*Z*)-isomer could not be isolated in pure state.

## Methods

The isomerizations were carried out in thick-walled 100  $\mu$ l ampoules in 1M solutions in benzene, chlorobenzene or bromobenzene. Mercury(II) acetate (10% m/m) was added as catalyst. The (*Z*)-isomers were identified as peaks having identical mass spectrum with the (*E*)-isomers. The GC analysis of pentenones used 5% SE XE-60, that of methoxy- and chlorobutenones used 20% Carbowax on Chromosorb 0.1–0.12 mm.

The following bond lengths (10<sup>-10</sup> m) were used for the energy calculations: C=C 1.35, =C-H 1.09, CH<sub>3</sub>-C= 1.49, C=O 1.22, =C-CO 1.47 (ref.<sup>23</sup>), CH<sub>3</sub>-CO 1.51 (ref.<sup>24</sup>); Cl-C 1.73 (ref.<sup>25</sup>), CH<sub>3</sub>O 1.43, O=C= 1.36, CH<sub>2</sub>-H 1.105 (ref.<sup>26</sup>); the bond angles in degrees, CH<sub>3</sub>-C=C 122, =C-C-C 117.2, OC-C-H 110.17 (ref.<sup>24</sup>), H-C=C-(CO) 119.9, C=C-C 119.8, C-C=C(O) 123.27, (X)-C=C-H 122.8 (ref.<sup>23</sup>), =C-C-H 109.5, C-O-C 116, O=C-C 127.7 (ref.<sup>26</sup>), Cl-C=C 126 (ref.<sup>27</sup>).

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