(*E*—*Z*)-ISOMERISATION OF CHLOROOLEFINS*

Miloš PROCHÁZKA, Jindřiška ADAMCOVÁ and Miloš PALEČEK
Department of Organic Chemistry,
Charles University, 128 40 Prague 2

Received December 4th, 1978

Equilibrium constants for the (*E*—*Z*)-isomerisation of the compounds R—CH=CH—Cl were determined and the experimental values compared with energy differences, calculated by the CNDO/2 method.

The preponderance of (Z)-isomers in the equilibrium between (*E*)- and (Z)-1,2-disubstituted ethenes represents a hitherto unexplained theoretical problem; this phenomenon was observed particularly in the series of halogeno olefins[1,2]. Therefore, we investigated the (*E*—Z)-equilibria for a series of chloro derivatives and tried to interpret them by calculations. Table I contains the hitherto known equilibrium data in the X—CH=CH—Cl series. In some cases the thermodynamic values are also known: *e.g.* for (Z)-1,2-dichloroethene[5,12] (the simplest case) $\Delta H^{\circ}_{f,298}$ 1·88 kJ . mol^{-1}, $\Delta G^{\circ}_{f,298}$ 24·36 kJ mol^{-1}; for the (*E*)-isomer $\Delta H^{\circ}_{f,298}$ 4·18 kJ mol^{-1}; $\Delta G^{\circ}_{f,298}$ 26·58 kJ mol^{-1}. Using spectral data, Pitzer and Hollenberg[13] calculated ΔH°_{0} −2·1 kJ mol^{-1} and assumed that the higher stability of the (Z)-isomer is caused by the attractive resonance interaction between the halogen atoms. An attempt to derive the repulsive van der Waals potentials from dipole moments of analogous compounds completely failed[14,15]. According to LCAO-MO calculation, the (Z)-isomer of 1,2-dichloroethene[16] is more stable and the C=C bond strength in both the isomers is different. Similarly, Boegel and Rasch[17] calculated $\Delta E(Z-E)$ to be −3·6 kJ mol^{-1} and 1·3 kJ mol^{-1}, using the respective CNDO/2 (*spd*-orbitals) and EHT MO methods. These calculations were in good agreement with the experimental value of −2·1 kJ mol^{-1}. However, on the basis of the population analysis and Wiberg indexes, the authors claim an overall repulsive interaction between the Cl··· Cl atoms. Another possible explanation of the preponderance of the (Z)-isomers are long-range interactions through bonding orbitals, through-space interactions or interactions of the charge transfer type affecting the bonding state of the molecule; *e.g.* Epiotis and collaborators[20] try to find explanation in the attractive interaction between the *p*-orbitals of hetero atoms of of the CH_3 group under formation of a cycle. Both isomers of 1,2-dichloroethene have been found to have planar geometry with a small but definite difference in bond lengths[18,19]. The barriers to rotation around the CH_3—C= bond in the (*E*)- and (*Z*)-isomers of 1-chloropropene are different[21,22] (being 9·08 kJ mol^{-1} and 2·6 kJ mol^{-1}, respectively).

We studied the (*E*–*Z*)-isomerisation in the series R—CH=CH—Cl where R is C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$ and C_6H_5, in order to gain information on steric effects, and calculated the energy differences by the CNDO/2 method[23] (with *sp* and partially *spd* orbitals). The results of the iodine-catalyzed isomerisations are given in Table II. The position of the equilibrium is determined decisively by the steric factor, which manifests itself by the coulombic repulsive term. In the case of 1-chloro-3-methyl-1-butene, the isomerisation with iodine leads to a complicated sequence of reactions, involving in addition to the (*E*–*Z*)-isomerisation also prototropic isomerisation, position isomerisation of halogen and hydrogenation–dehydrogenation reactions. These reactions are probably induced by the arising hydrogen iodide. Using shorter reaction time, the ratio of (*Z*)- and (*E*)-isomers is (according to kinetic data) 0·57. Therefore, we tried other catalysts such as $Hg(OAc)_2$, $PdCl_2$, $Fe(CO)_5$, NO, $(tert\text{-}C_4H_9)_2S_2$, Br_2 with irradiation, $RCl[(C_6H_5)_3P]_3 + H_2$. Of these catalysts only irradiation with tungstene lamp in the presence of bromine gave good results; the rhodium catalyst led to a prototropic equilibrium (98 ± 1% of 1-chloro-3-methyl-2-butene and 2% of 4-chloro-2-methyl-1-butene at 453 K). From this isomerisation one can deduce a high thermodynamic stability of the non-allylic isomer. The similar equilibrium values for R = CH_3, C_2H_5 and CH_2CN show preponderance of a conformer of the type *I* such as known in 1-propene, 1-butene, acetone and other compounds[22].

The quantum chemical calculations were carried out using geometric parameters found experimentally for analogous compounds (see Experimental). As the optimum conformation of 1-chloro-1-butenes, 1-chloro-3-methyl-1-butenes and 1-chloro-3,3-dimethyl-1-butenes we chose the form with maximum number of staggered (*ac*) conformations in the alkyl group[24], for other compounds a whole computation of the barrier to rotation was carried out and the optimum conformation of the groups derived.

From the point of geometry, 1,2-dichloroethene represents the simplest case: for this compound we performed the calculations with *sp*- as well as *spd*-bases (Santry–Segal parameterisation[25]). In the *sp*-basis the (*Z*–*E*) energy difference was calculated to be −0·4 kJ mol^{-1} for the one-center and 2·5 kJ mol^{-1} for the two-center part; thus the total value of ΔE is +2·1 kJ mol^{-1} in favour of the (*E*)-isomer. In the *spd* basis, ΔE amounts to −5·6 kJ mol^{-1} (the experimental value is −2·1 kJ mol^{-1}); however, application of this basis to a more extended series of compounds shows that this result represents rather a fortuitous agreement between the theoretical and experimental value. In the *sp*-basis, the following energy differences of the two-center component were found: for the interaction $(Cl^{(1)} \cdots C^{(2)}) = (Cl^{(5)} \cdots C^{(3)})$, total for both −6·2 kJ mol^{-1}; for $(C^{(2)} \cdots H^{(4)}) = (C^{(3)} \cdots H^{(6)})$ = −8·4 kJ mol^{-1}, $(Cl^{(1)} \cdots C^{(3)}) = (Cl^{(5)}{=}C^{(2)})$ = 17·4 kJ mol^{-1}, $(Cl \cdots Cl)$ only −0·5 kJ mol^{-1}, and

$(C^{(2)}{=}C^{(3)}) = 1{\cdot}2$ kJ mol^{-1}. With the *spd*-basis, the main difference in the one-center part concerns the charge on the chlorine atoms; in the prevailing two-center component which determines the greater stability of the (*Z*)-isomer, the following energy differences were calculated: $(Cl^{(1)}{\cdots}C^{(3)}) = (Cl^{(5)}{\cdots}C^{(2)})$ total $= 1{\cdot}25$; $(H^{(4)}{\cdots}H^{(6)}) = 8{\cdot}0$, $(C^{(2)}{\cdots}H^{(4)}) = (C^{(3)}{\cdots}H^{(6)})$ total $= -8{\cdot}0$. The lower repulsive Cl···Cl interaction in the (*Z*)-isomer is decisive (for the (*Z*)-isomer 8·6, for the (*E*)-isomer 29·9 kJ mol^{-1}; the difference being thus $-21{\cdot}35$ kJ mol^{-1}) because in the (*Z*)-isomer there is a significant resonance energy contribution which is the result of participation of *d*-orbitals. However, if we compare this agreement of theory with experiment with the results of calculations performed for methyl 3-chloropropenoate or 1-chloro-1-propene, the question of utilisation of *d*-orbitals and their parameterisation is very questionable.

TABLE I

Equilibria between the Stereoisomeric Chloroalkenes X—CH=XH—Cl

X	$K_{Z/E}$	T, K	Conditions	Ref.	Note
CH_3	3·08	303	l. phase	3	
	2·52	423	g. phase	4	[a]
F	2·06	474	g. phase	1	[b]
	2·33	473	g. phase	2	
Cl	1·55	562	g. phase	1	[c]
	1·65	488			
	1·70	573	g. phase	6	[d]
OC_2H_5	4·52	298	octane	7	[e]
SCH_3	1·6	443	1,4-dioxane	8	
$COOCH_3$	0·15	475	1,4-dioxane	9	
CH_2Cl	1·3	303	l. phase	3	[f]
	2·75	303	t-C_4H_9OH	10	[g]
CH_2CN	2·75	303	t-C_4H_9OH	10	
	2·16	313	CH_3CN	11	
CN	1·32	353	l. phase	3	

[a] ΔH°_{0} 3·18 kJ mol^{-1}; [b] ΔH°_{615} 3·25 kJ mol^{-1}, ΔS^{0}_{615} 0·87 JK^{-1} mol^{-1}; [b] ΔH°_{0} 2·7 kJ mol^{-1}, ΔS°_{540} 1·25 JK^{-1} mol^{-1}, ΔS°_{731} 2·05 JK^{-1} mol^{-1}; [d] less accurate value; [e] ΔH°_{0} —2·76 kJ mol^{-1}, ΔS 3·26 JK^{-1} mol^{-1}; [f] because of the catalyst used (Br_2 + UV light), a possible shift towards photochemical equilibrium cannot be excluded; [g] less accurate value from the base-catalysed prototropic equilibrium.

TABLE II

Equilibrium Data on the (*E*—*Z*) Isomerisation of R—CH=CH—Cl

R	*T*, K	$K_{Z/E}$	ΔG	ΔH	ΔS
			kJ mol^{-1}		JK^{-1} mol^{-1}
C_2H_5	443	2·10	—2·73	—	—
	463	1·87	—2·41		
$(CH_3)_2CH$	318	0·65[a]	1·14	—	—
	453	0·57[b]	2·11		
$(CH_3)_3C$	464	0·112	8·43	19·6	24·1
	483	0·138	7·96		
C_6H_5	453	0·258	5·10	18·6	30·0
	473	0·322	4·46		

[a] Irradiation with 100 W tungsten lamp in the presence of Br_2; the value is less accurate because of simultaneous polymerization; [b] catalysis with iodine, the value derived from kinetic data.

TABLE III

Calculation of Barrier to Rotation in 1-Chloro-1-propene (kJ mol^{-1})

Angle of planes C=C—C and =C—CH	Part		ΔE
	one-center	two-center	
	(*E*)-isomer		
0° (*sp*)	2 505·15	—11 252·65	—8 746·5
30°	2 505·9	—11 249·5	—8·743·7
60° (*sc*)	2 506·5	—11 247·4	—8 740·9
	(*Z*)-isomer		
0° (*sp*)	2 508·6	—11 252·8	—8 744·2
30°	2 508·9	—11 252·4	—8 743·5
60° (*sc*)	2 509·2	—11 251·7	—8 742·5

TABLE IV

Bonding Energy in the Halogeno Olefins (kJ mol^{-1})

Compound	Part		ΔE
	one-center	two-center	
1-Chloro-1-butene			
(*Z*)-Isomer	3 335·1	—15 360·5	—12 025·4
(*E*)-Isomer	3 331·3	—15 359·1	—12 027·8
Difference	3·8	—1·4	2·4
1-Chloro-3-methyl-1-butene			
(*Z*)-Isomer	4 153·8	—19 449·6	—15 295·8
(*E*)-Isomer	4 149·6	—19 448·1	—15 298·5
Difference	4·2	—1·5	2·7
1-Chloro-3,3-dimethyl-1-butene			
(*Z*)-Isomer	4 959·1	—23 493·9	—18 534·9
(*E*)-Isomer	4 953·3	—23 501·4	—18 548·1
Difference	5·7	7·5	13·2

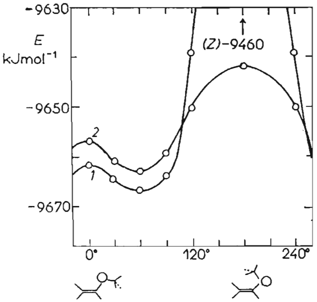

FIG. 1

Plot of Calculated Energies *vs* Torsion Angle around the C—O Bond in (*E*)- and (*Z*)-1-Methoxy-2-chloroethene

Curves: *1* (*Z*)-isomer, *2* (*E*)-isomer.

For 1-chloro-1-propene we calculated the barrier to rotation (*sp*-orbitals) of the CH_3 group for the angles 0° (*sp*-position of the hydrogen atom and C=C), 30° and 60° (*sc*). In both the (*E*)- and (*Z*)-isomers the eclipsed (*sp*) conformation prevails (Table III); the analysis of the bonding components in the 0° and 60° conformations shows that in the (*E*)-isomer the difference between the two-center component interactions does operate (Fig. 1).

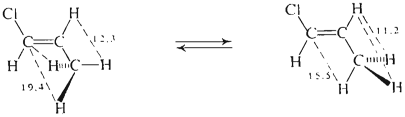

FIG. 2

Significant Differences between Interactions in the 0° and 60° Conformations of (*E*)-1-Chloro-1-propene (k J mol^{-1})

FIG. 3

Numbering of Atoms in Isomeric Chlorobutenes

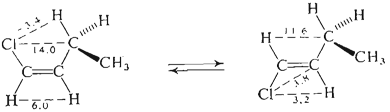

FIG. 4

Differences in the Two-Center Interactions in (*Z*)- and (*E*)-1-Chloro-1-butene

(The energy differences between the interactions, (*Z*—*E*), are given for the isomer in which the particular interaction is stronger)

The barrier to rotation in the (*E*)-isomer was calculated to be 5·6 kJ mol^{-1} (experimental value 9·08 kJ. mol^{-1})[21,22]. In the (*Z*)-isomer the energy difference between the conformations is lowered by the attractive Cl···H interaction in the eclipsed rotamer (−4·0 kJ mol^{-1}); the calculated barrier is 1·7 kJ mol^{-1} (the experimentally found value is 2·6 kJ mol^{-1})[22]. The found optimum conformation falls into line with the generally higher stability of eclipsed forms in the compounds of the type $CH_3—C=X$, *e.g.* in propene, acetone or acetaldehyde[26]. The energy difference between the most stable conformations of 1-chloro-1-propene, ΔE, is 2·3 kJ mol^{-1} (one-center part +3·4, two-center part −1·1 kJ mol^{-1}). With increasing temperature there is an increase in population of the *sc* conformations for which ΔE was calculated to be −1·6 kJ mol^{-1} in favour of the (*Z*)-isomer.

For 1-chloro-1-butene, 1-chloro-3-methyl-1-butene and 1-chloro-3,3-dimethyl-1-butene (Table IV) the calculations show that the (*E*)-isomers predominate (ΔE 2·4, 2·7 and 13·2 kJ mol^{-1}, respectively). In the one-center part, the energy differences between the (*E*) and (*Z*) isomers concern the atoms Cl and $H^{(7)}$, $C^{(6)}$ and $H^{(5)}$ (Fig. 2); the two-center interactions in chlorobutene and chloromethylbutene compensate

TABLE V

Significant Energy Differences in the Two-Center Component for Stereoisomeric 1-Methoxy-2-chloroethenes (>3 kJ mol^{-1}) for Conformations with the $C—OCH_3$ Torsion Angle 60° (*ac*) and 0° (*ap*) (kJ mol^{-1})

Interaction	(*Z*)-Isomer			(*E*)-Isomer		
	60°	0°	difference	60°	0°	difference
$O^{(6)}\cdots C^{(2)}$	68·1	85·3	—17·2	69·8	76·8	—17·0
$C^{(7)}\cdots C^{(2)}$	11·9	— 3·3	15·2	11·8	— 3·2	15·0
$H^{(4)}\cdots O^{(6)}$	43·4	32·9	10·5	43·9	33·3	10·6
$H^{(4)}\cdots C^{(7)}$	6·7	16·7	—10·0	6·9	17·2	—10·3
$C^{(3)}—O^{(6)}$	— 1 881·9	— 1 889·9	8·7	— 1 879·5	— 1 888·5	8·9
$C^{(7)}\cdots C^{(3)}$	— 118·8	— 108·3	—15·5	— 118·3	— 103·3	—15·0
$C^{(3)}\cdots H^{(10)}$	3·0	7·5	— 4·5	3·1	7·5	— 4·4
One-center component	3 077·7	3 073·0	4·7	3 080·3	3 077·5	2·8
Two-center component	—12 745·4	—12 734·6	—10·8	—12 743·8	—12 734·6	— 9·2
Total energy	— 9 667·7	— 9 661·6	— 6·1	— 9 663·5	— 9 657·1	— 6·4

TABLE VI

Bonding Energy Differences between the Two-Center Components of 1-Methoxy-2-chloroethenes (>2 kJ mol^{-1})

Interaction	(*Z*)-Isomer	(*E*)-Isomer	Difference
$C^{(2)}\cdots O^{(6)}$	68·1	59·6	8·3
$C^{(2)}$—Cl	— 989·8	— 994·5	4·6
$C^{(3)}\cdots$Cl	44·3	40·9	2·5
$H^{(4)}\cdots H^{(5)}$	11·7	8·1	3·6
$C^{(2)}=C^{(3)}$	— 2 865·9	— 2 860·6	—5·4
$C^{(2)}\cdots H^{(4)}$	19·4	24·0	—4·6
$C^{(2)}$—$H^{(5)}$	— 1 144·8	— 1 140·4	—4·5
One-centre component	3 077·7	3 080·3	—2·6
Two-centre component	—12 745·4	—12 743·8	—1·6
Total energy	— 9 667·7	— 9 663·5	—4·2

TABLE VII

Experimental (ΔE_{exp}) and Calculated (ΔE_{calc}) Energy Differences between (*Z*)- and (*E*)-Isomers of X—CH=CH—Cl (kJ mol^{-1})

X	ΔE_{exp}	ΔE_{calc}	$\Delta E_{exp} - \Delta E_{calc}$
Cl	—2·2	2·1	—4·3
CH_3	—3·2	2·3	—5·5
C_2H_5	—2·8[a]	2·4	—4·8
$(CH_3)_2CH$	—2·1[a]	2·7	—0·6
$(CH_3)_3C$	19·6	13·2	6·4
OC_2H_5	—2·8	—4·2[b]	1·4
SCH_3	—3·0	2·2	—5·2
$COOCH_3$	10·8	8·1	2·7
CN	—0·8[a]	—0·1	—0·7

[a] ΔG^{0}_{450}; [b] calculated for the analogous 1-methoxy-2-chloroethene.

each other whereas in chlorodimethylbutene the coulombic repulsions operate significantly, even in optimum conformation (Fig. 5). The significant differences between two-center interactions in 1-chloro-1-butene, 1-chloro-3-methyl-1-butene, and 1-chloro-3,3-dimethyl-1-butene are given in Figs 3–5.

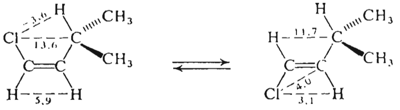

FIG. 5

Differences in Two-Center Interactions in 1-Chloro-3-methyl-1-butenes

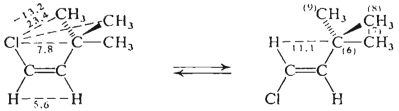

FIG. 6

Differences in Two-Center Interactions in 1-Chloro-3,3-dimethyl-1-butenes

(The antibonding interaction between the chlorine atom and the $C^{(8)}$ and $C^{(9)}$ carbons (total 23·4 k J mol^{-1}) is partly compensated by bonding interaction of the nearest hydrogens of both methyl groups with the chlorine atom (total —13·2 k J mol^{-1}))

For 1-methoxy-2-chloroethenes, the plot of calculated conformational energies against torsion angle (Fig. 6) shows that at 300 K the (*E*)-isomer has one energy maximum in the region 60 ± 15° (*ac*-conformation) and two minima at about 0° (*ap*-rotamer) and 180° (*sp*-form). The calculated barriers to rotation are 6·4 and 21·6 kJ mol^{-1}; these values allow at 300 K interconversion of the conformers. The (Z)-isomer exhibits a similar dependence of energy on torsion angle but the barriers to rotation amount to 6·1 and 207 kJ mol^{-1}, allowing thus at 300 K only a libration within the ±120° limits. Consequently, we can expect a significant entropic change with increasing temperature. Comparison of the 0°, 60° and 120° rotamers reveals that the energy difference is caused by significant differences in the two-center energy component (Table V).

It follows from the differences in interaction energies that in both the (*E*)- and (*Z*)-isomer the interaction energy changes are similar and that the substituent at the $C^{(2)}$ carbon (*i.e.* Cl) is not involved in the interactions. The interaction energies in the *ac* (60°) and *sc* (120°) conformations indicate an increase in the interactions $C^{(2)} \cdots C^{(7)}$ and $C^{(3)} \cdots C^{(7)}$, $C^{(7)} \cdots H^{(4)}$ and $C^{(3)} \cdots H^{(10)}$ and a decrease in the C=C bond bond strength, approximately the same in both isomers. In addition, in the (*Z*)-isomer the $C^{(7)} \cdots Cl$ and $H^{(10)} \cdots Cl$ interactions ($-20{\cdot}5$ and $+6{\cdot}0$ kJ mol^{-1}, respectively) steeply increase which leads to increasing stability of the (*E*)-isomer.

Analysis of the difference between the two-center components of bond energies in the optimum-*ac*-conformations (the angle between the planes is 60°) shows that the difference ΔE has several substantial components (>2 kJ mol^{-1}) which are listed in Table VI. The non-bonding interactions of the chlorine atom contribute only insingificantly and the two-center interactions fairly compensate each other. Particularly unexpected is the small contribution of the $Cl \cdots O^{(6)}$ interaction ((*Z*)-isomer 23·7 kJ mol^{-1}, (*E*)-isomer 25·6 kJ mol^{-1}) since in the (*Z*)-isomer (difference $-1{\cdot}9$ kJ mol^{-1}) the greater repulsion is compensated by resonance.

For 1-methylthio-2-chloroethene the optimum conformations were calculated[27] to be those with an antiperiplanar position of the CH_3—S and C=C bonds, the difference between the bonding energies being 2·2 kJ mol (calculation with *sp*-orbitals) and $-5{\cdot}0$ kJ mol^{-1} (with *spd*-orbitals). In the (*E*)-isomer there is a relatively free rotation at 300 K, whereas the interaction, present in the (*Z*)-isomer, allows only libration within 0 ± 150° limits.

For methyl 3-chloropropenoate, according to the CNDO/2 (*sp*-orbitals) calculation[28], the C=C—C=O *s-cis* conformation has the highest bonding energy, the energy difference being 8·1 kJ mol^{-1} in favour of the (*E*)-isomer (more stable). An analogous calculation with *spd*-orbitals affords an energy difference of $-26{\cdot}3$ kJ . . mol^{-1} which does not agree with the experimental value.

3-Chloropropenonitrile[29] exists in only one conformation. The total bonding energy difference between (*E*)- and (*Z*)-isomers of 3-chloropropenonitrile has been found to be $-0{\cdot}1$ kJ mol^{-1}. Analysis of the two-center part revealed an approximate accord between the bonds, except for the C=C bond which in the (*Z*)-isomer is stronger by 2·1 kJ mol^{-1}. The interactions between the more distant atoms compensate each other, resulting in a difference of 0·8 kJ mol^{-1} between the two isomers. The experimentally found[3] value is $\Delta G_{353} = -0{\cdot}8$ kJ mol^{-1}.

If we now compare the calculated values of ΔE (*sp*-basis set) with the ΔH (or ΔG) values, determined experimentally from the equilibria (Table I and II), we find that the CNDO/2 calculation obviously overestimates the interactions of the more distant atoms. The total calculation gives values shifted to higher bonding energies in the (*E*)-isomers. However, the calculations undoubtedly show what are the substantial effects and what is their relative extent. The pertinent comparison is performed in Table VII.

EXPERIMENTAL

The purity of compounds was checked by gas-liquid chromatography under conditions used for the isomerisations. The IR spectra were taken on a UR-10 (Zeiss, Jena) spectrophotometer (carbon disulfide). The ^{1}H-NMR and ^{13}H-NMR spectra were measured on a Jeol FX-60 instrument (internal standard tetramethylsilane, δ scale).

(*E*)- and (*Z*)-1-chloro-1-butenes were prepared in 94% yield by the reaction of 1,1-dichlorobutane[30] with potassium hydroxide in 2,2′-oxydiethanol; the mixture of isomers was separated by distillation on a column (40 TP). (*E*)-Isomer. b.p. 68·9°C/98·1 kPa; IR spectrum, cm^{-1}: 780, 935, 1 660, 2 860, 2 880, 2 980, 3 030. (*Z*)-Isomer was prepared by preparative gas-liquid chromatography (5 m column, diameter 8 mm, 55°C, 8% Apiezon on ground porous tile); b.p. 61°3/99·2 kPa. IR spectrum, cm^{-1}: 710, 1 640, 2 980, 2 883, 3 025.

Under analogous conditions, elimination of hydrogen chloride from 1,1-dichloro-3-methylbutane[31] afforded a mixture of stereoisomeric 1-chloro-3-methyl-1-butenes[32] in 48% yield. Distillation and gas-liquid chromatography at 70—80°C gave the (*Z*)-isomer, b.p. 78 to 79·5°C/99·3 kPa; IR spectrum, cm^{-1}: 724, 1 170, 1 388, 1 635, 3 015. ^{1}H-NMR spectrum: 1·01 d, $J = 6·35$ Hz (($CH_3)_2$), 2·93 m (—CH—); ABX system: $J_{AB} = 7·3$ Hz, $J_{AX} = 9·1 \pm 1$ Hz, $J_{BX} = 0·8$ Hz. ^{13}C-NMR spectrum: 21·7 (C—4, C—5); 26·7 (C—3); 115·7 (C—2); 138·6 (C—1). For C_5H_9Cl (104·6) calculated: 57·4% C, 8·7% H, 33·9% Cl; found: 57·2% C, 8·88% H, 34·0% Cl. (*E*)-Isomer b.p. 88·5°—90°C/99·3 kPa; IR spectrum, cm^{-1}: 938, 1 388, 1 634, 3 020. ^{1}H-NMR spectrum: 1·01 d, $J = 6·83$ Hz (($CH_3)_2$); 2·3 m (—CH—); $J_{AB} = 13·2$ Hz. ^{13}C-NMR spectrum: 21·9 (C—4, C—5); 30·4 (C—3); 115·2 (C—2); 140·6 (C—1).

A mixture of (*E*)- and (*Z*)-1-chloro-3,3-dimethyl-1-butene was prepared analogously from 1,1-dichloro-3-dimethylbutane[31] in 72% yield. Distillation on a column (50 TP) afforded the pure (*E*)-isomer, b.p. 105·7°C/98 kPa. ^{1}H-NMR spectrum: 1·05 s (CH_3), 5·92 s (CH=CH). IR spectrum, cm^{-1}: 943, 1 368, 1 395, 1 660, 2 878, 2 970, 3 018. The lower-boiling fraction, b.p. 100·8—102°C/98·5 kPa, consisted of 54% (*Z*)-isomer and 46% (*E*)-isomer and was not separable by preparative gas-liquid chromatography. For $C_6H_{11}Cl$ (118·6) calculated: 60·7% C, 9·3% H, 28·9% Cl; found: 60·5% C, 9·1% H, 30·2% Cl.

(*E*)- and (*Z*)-1-chloro-2-phenylethenes were prepared in 80% yield by simultaneous dehydrohalogenation and decarboxylation of 2,3-dichloro-3-phenylpropanoic acid according to ref.[33,34]. Fractionation on a column (50 TP) afforded the (*Z*)-isomer, containing 6·9% of the (*E*)-isomer; b.p. 75·1—75·4°C/0·8 kPa; 198°C/99 kPa (reported b.p. 60—64°C/2·4 kPa); IR spectrum, cm^{-1}: 693, 725, 775, 850, 1 350, 1 628, 3 035, 3 085. The (*E*)-isomer was obtained from the fraction boiling at 80°—100°C/1·1 kPa by crystallisation at —20°C and recrystallisation at —60°C from light petroleum; b.p. 202°C/99 kPa; IR spectrum, cm^{-1}: 693, 740, 818, 938, 1 618, 1 078, 1 250, 3 036, 3 085 (in accord with the reported[35] spectrum). For C_8H_7Cl (138·6) calculated: 69·3% C, 5·1% H, 25·6% Cl; found: 69·4% C, 5·2% H, 25·4% Cl.

The isomerisations were carried out in thick-walled 100 µl ampoules at 433—483 K with 0·35—1·0M solutions of the compounds in chlorobenzene, using 2·5% (wt) of iodine as catalyst. After cooling, the ampoules were opened, the iodine removed by sodium thiosulfate, and the mixture was analysed by gas-liquid chromatography. Aliphatic compounds were analyzed using 20% Squalane on Chromosorb W 80/100 at 50°C, chlorophenylethenes were chromatographed on 10% Apiezon K on Chromaton N-AW-DMCS at 115°C. The iodine-catalysed isomerisation of (*E*)- and (*Z*)-1-chloro-3-methyl-1-butene at 453 K affords a mixture of compounds which can be separated on a column of graphitized coal Sterling MT 0·2—0·3 mm (1·5 m, 85°C). Gas-liquid chromatography — mass spectrometry (graphitized coal, 150 cm column, 3 mm diameter, 80°C, 45 ml He min^{-1}) showed that the preparative isomerisation (2·5% iodine-180°C, 12 h) afforded 11·7% of a mixture of 2-methyl-2-butene, 3-methyl-1-butene, 2-methyl-

-1-butene and 1,1-dimethylcyclopropane, 11·1% of 2-chloro-2-methylbutane, 0·4% of 1-chloro-3-methyl-1-butene, 19% of 2-chloro-3-methylbutane, 3·6% of 2-methyl-1-chlorobutane, 16% of 3-methyl-1-chlorobutane and 22·5% of unidentified compounds. Therefore other catalysts were tried: 2·5% Hg $(OAc)_2$ in tetrahydrofuran (4 h at 180°C), $PdCl_2$, NO in chlorobenzene, $Fe(CO)_5$ (14 h at 453 K), $(tert\text{-}C_4H_9)_2S_2$ + UV light. Treatment with tris(triphenylphosphine)-rhodium chloride, in the presence of a small amount of hydrogen at 493 K for 50 h led to an equilibrium mixture containing 98% of 1-chloro-3-methyl-2-butene and 2% of 4-chloro-2-methyl-1-butene. Shorter reaction times showed that also the (*E*—*Z*)-isomerisation had taken place; this isomerisation, however, was a far slower reaction and equilibrium was never achieved. Treatment with bromine and irradiation with tungsten lamp (11 h) at 318 K resulted in (*E*—*Z*)-isomerisation, the (*Z*/*E*) ratio being 0·66.

For both (*E*) as well as (*Z*) stereoisomers, following bond lengths were used in the calculations (10^{-10} m): C—C 1·54; =C—C 1·51; =C—Cl 1·72; =C—H 1·08; =C—O 1·36; C=C—OR 1·44; C=C—CN 1·445; C≡N 1·16; C—H 1·09; =C—C=O 1·46; —C=O 1·22; CO—OR 1·36; C—OR 1·43. In all cases except =C—SR (125·9°), the angles Cl—C=C and C=C—R were taken as 122°, the =C—S—C angle 104·5°; other angles were taken as 120°C or tetrahedral.

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Translated by M. Tichý.