The Molecular Structure of 3-*tert*-Butyl-4,4-dimethyl-2-pentenal (3,3-Di-*tert*-butylpropenal)[‡]

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The highly strained conjugated aldehyde 3-*tert*-butyl-4,4-dimethyl-2-pentenal (3,3-di-*tert*-butylpropenal; abbreviated D33; **4**) has been prepared, and its molecular structure and conformation have been studied experimentally by the gas electron diffraction method and by theoretical ab initio (HF/6-31G*) calculations. The propenal skeleton assumes an *anti* conformation, and the steric strain is primarily manifested in the following structural details: The C=C–C angle is substantially larger than normal [GED: 132.6(7)°; HF/6-31G*: 132.5°]; the (*Z*)-oriented *tert*-butyl group is twisted to a nearly staggered position relative to the C=C double bond, forming a cogwheel system with the other *tert*-butyl group, which has the normal eclipsed conformation relative to C=C; the C^3–C_{tBu} (formally sp^2–sp^3) bonds are elongated compared to those in unstrained compounds, and are longer than the (formally sp^3–sp^3) C–CH_3 bonds.

Introduction

When two *tert*-butyl groups are bonded to the same carbon atom in a molecule, nonbonded repulsions between the two substituent groups will be very large if normal geometry parameters are to be preserved. This is the case whether the substituted carbon atom is saturated ('sp^3-hybridized') or unsaturated ('sp^2-hybridized'), although the strain is expected to be larger in the case of a tetrahedral carbon atom, because of the smaller reference $C_{tBu}-C-C_{tBu}$ angle, forcing the substituents closer together. Generally, it is energetically favorable for a sterically strained molecule to distribute the strain in smaller portions over larger parts of the molecule, rather than concentrating it as one particular type of strain, such as nonbonded repulsion. The structures of *gem*-di-*tert*-butyl organic compounds should therefore be expected to show unusual structural properties as a result of distributing the steric strain as effectively as possible.

The structures of several saturated *gem*-di-*tert*-butyl compounds have been studied; one example is gaseous di-*tert*-butylmethane,[2] in which the steric strain is manifested in an unusually large $C_{tBu}-C-C_{tBu}$ angle [128(6)°], together with other minor geometrical effects. In tri-*tert*-butylmethane,[3] the $C_{tBu}-C-C_{tBu}$ angle is only enlarged to 116°, because of the additional steric strain arising from the third *tert*-butyl substituent. In this case, however, nonbonded repulsions are reduced through elongation of the three central $C-C_{tBu}$ bonds, to 1.611(5) Å, the longest C−C bonds measured by electron diffraction for an acyclic hydrocarbon. The extreme congestion is also reflected in the $C_{Me}-C_{tBu}-C_{Me}$ and $C_{tBu}-C_{Me}-H_{Me}$ angles of the *tert*-butyl groups [105.7(2) and 114.2(1.0)°, respectively].

Even though the steric strain is expected to be somewhat reduced in an unsaturated *gem*-di-*tert*-butyl alkene, compared to that in an analogous saturated molecule, it is large enough to have a major effect on the structural and conformational properties.[4,5] In this context, it is of interest to note that, despite numerous efforts, nobody has so far succeeded in synthesizing the doubly *gem*-di-*tert*-butyl-substituted unsaturated molecule tetra-*tert*-butyl-ethene.[6]

The steric strain in several di-*tert*-butyl-substituted 1,3-butadienes has been studied experimentally,[1,7] as well as theoretically.[8] Calculated energies for the nine different di-*tert*-butyl-substituted 1,3-butadienes showed that the *gem*-di-*tert*-butyl-substituted compound is clearly the most highly strained one.[8] The structure and conformation of 1,1-di-*tert*-butyl-1,3-butadiene (D11) have been studied experimentally by gas electron diffraction,[1] and some interesting structural effects − arising from the steric strain − were revealed. In this paper we present results obtained from a study of a molecule closely related to D11: namely 3,3-di-*tert*-butylpropenal (D33, **4**). We chose to study this molecule because we wanted to obtain more information on sterically strained *gem*-di-*tert*-butyl unsaturated compounds, particularly on α,β-unsaturated carbonyl compounds because of the general importance of this class of organic compounds. Furthermore, **4** is the starting building block of most of our recently synthesized α,ω-tetra-*tert*-bu-

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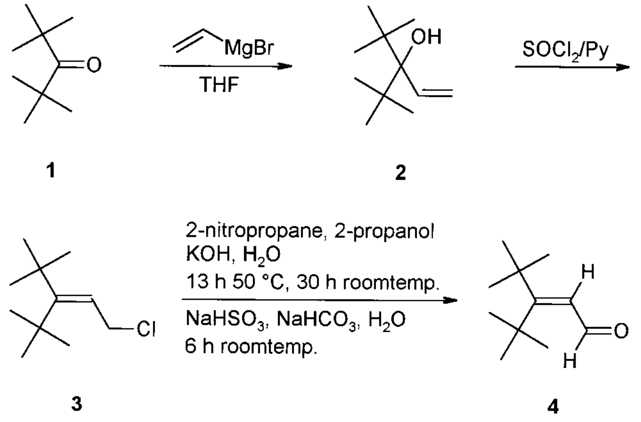
tylated oligo- and polyenes[9] and hence a description of its preparation is given.

Synthesis and Gas Electron Diffraction

Synthesis

The synthesis of **4** was carried out as outlined in Scheme 1. Treatment of 2,2,4,4-tetramethyl-3-pentanone (di-*tert*-butyl ketone, **1**) with vinylmagnesium bromide in tetrahydrofuran produced the allyl alcohol **2** (90% yield), which underwent allyl rearrangement in the presence of thionyl chloride in pyridine, yielding the primary halide **3** (58%).



Scheme 1. Preparation of 3-*tert*-butyl-4,4-dimethyl-2-pentenal (D33, **4**)

Conversion of the chloromethyl group in **3** into a formyl function was accomplished by treating the halide with 2-nitropropane in 2-propanol in the presence of potassium hydroxide. After hydrolytic workup, compound **4** was isolated in 66% yield and characterized by the usual spectroscopic methods (see Experimental Section). According to NMR analysis the aldehyde was more than 98% pure.

Gas Electron Diffraction Recordings

Electron diffraction diagrams were recorded with a Balzer Eldigraph KD-G2 unit,[10,11] using an r^3-sector and Kodak Electron Image plates. The nozzle tip temperature during the experiments was 66.0 °C. The electron diffraction wavelength was 0.058401 Å, calibrated against the diffraction pattern of gaseous benzene. Electron diffraction photographs were recorded at nozzle-to-plate distances of 498.68 mm (5 plates) and 248.80 mm (5 plates). The experimental data were treated in the usual way,[12] and the modification function used was $s.f_C^{-2}$. The complex scattering factors by Ross et al.[13] were used, while the inelastic factors employed were those of Tavard et al.[14] The experimental molecular intensity curve is presented in Figure 1.

Structure Study; Results and Discussion

Theoretical Calculations

Ab initio optimization calculations were carried out on **4**, using the GAUSSIAN94 program package,[15] at the HF/6-31G* level. The fully optimized minimum energy conformer has an *anti* orientation at the C1−C2 bond. In order to investigate whether other rotational minima at this bond were likely to be present, several HF/6-31G* calculations were carried out for fixed values of the C=C−C=O dihedral angle in the region 180−300° (for higher values of the dihedral angle it proved difficult to obtain convergence). The relative energies for 30° intervals − starting at 180° − were 0.0, 1.27, 4.08, 5.4, and 5.5 kcal mol^{-1}. In these calculations, only those parameters expected to be most strongly influenced by the rotation (C3=C2−C1 and C2−C1=O) were varied, while the other parameters were set equal to those relating to the fully optimized *anti* conformer. The calculated energy increases are therefore probably somewhat too large, but they indicate that gaseous D33 is conformationally homogeneous, and that the molecules have *anti* orientation of the conjugated system. Selected structural parameters obtained from the fully optimized HF/6-31G* calculation are presented in Table 1.

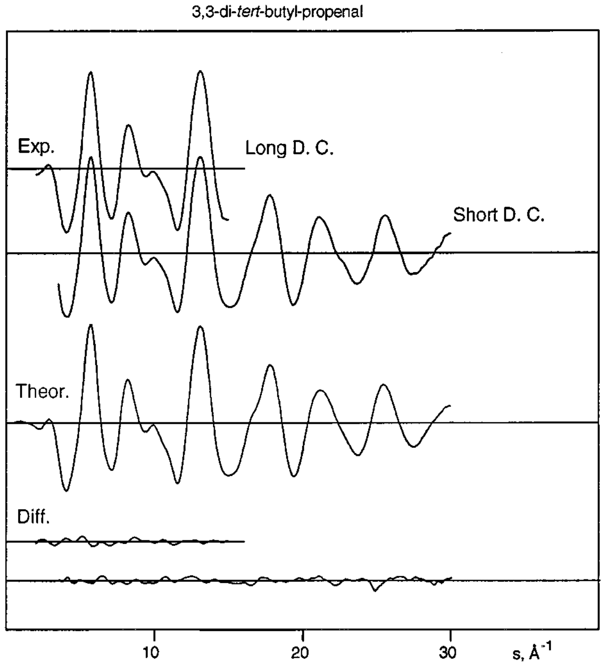


Figure 1. Experimental and theoretical molecular intensities for D33 (**4**) and the differences between the two curves

The atom numbering system used is illustrated in Scheme 2. In order to facilitate readability of the molecular model, only the hydrogen atoms at C1 and C2 are included, in addition to the carbon atoms.

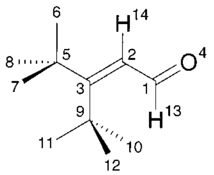
The vibrational amplitudes and shrinkage corrections of all interatomic distances in D33 were calculated using the program ASYM40,[16] and the Cartesian force constants − calculated by the GAUSSIAN94 program at the HF/6-31G* level − were applied as an initial force field. The scaling constants introduced to compensate for the well known overestimation of the calculated frequencies (due to neglect of electron correlation) were set equal to 0.893.[17]

The GED Study

In a large and complicated molecule such as D33, it is necessary to make some assumptions in the molecular

Table 1. Selected molecular structure parameters obtained for **4** (D33) by ab initio optimization calculations (HF/6-31G*); distances in Å, angles in degrees

C2=C3	1.3392	C3−C5−C6	112.7
C1=O4	1.1944	C3−C5−C7	109.6
C1−C2	1.4824	C3−C5−C8	113.0
C3−C5	1.5613	C3−C9−C10	109.9
C3−C9	1.5673	C3−C9−C11	117.4
C−CH_3	1.5446−1.5483	C3−C9−C12	109.1
		C2=C3−C5−C6	−6.8
		C2=C3−C5−C7	110.4
C3=C2−C1	132.5	C2=C3−C5−C8	−125.9
C2−C1=O4	120.4	C2=C3−C9−C10	54.2
C2=C3−C5	116.6	C2=C3−C9−C11	172.0
C2=C3−C9	120.7	C2=C3−C9−C12	−67.9
C3=C2−H14	119.6	C5−C3−C9	122.7
C1−C2−H14	107.9		
C2−C1−H13	120.5		
O4=C1−H13	119.0		



Scheme 2. Simplified molecular model of D33 (**4**), showing the numbering of the carbon atoms and the hydrogen atoms at C2 and C3

model used in the GED study. In this study the following assumptions were made, on the basis of the theoretical HF/6-31G* optimization results (for the numbering of the atoms see Scheme 2 above):

- The differences between the six C3−C−CH_3 angles were set equal to those calculated, using C3−C5−C6 as an independent parameter.
- All C−C−H_{Me} angles were fixed at the calculated values.
- The differences within each of the two sets of C2=C3−C−CH_3 dihedral angles were fixed at the calculated values, using C2=C3−C5−C6 and C2=C3−C9−C10 as independent parameters.
- All C−CH_3, C_{sp^3}−H and C_{sp^2}−H bonds were respectively set equal.
- C3−C5 and C3−C9 were linked together by the calculated bond difference.
- C2=C3−C5 and C2=C3−C9 were linked together by the calculated bond angle difference.

When these approximations were introduced in the D33 molecular model, 16 parameters were necessary in order to describe the geometry of the model, namely:

7 *bond lengths*: C1−C2, C2=C3, C=O, C3−C5, C−CH_3, C_{sp^3}−H, and C_{sp^2}−H.

6 *valence angles*: C3=C2−C1, C2−C1=O, C2=C3−C5, C3−C5−C6, C3=C2−H, and O=C−H.

3 *dihedral angles*: C3=C2−C1=O, C2=C3−C5−C6, and C2=C3−C9−C10.

The molecular structure of **4** was determined by GED, based on least-squares refinements of the molecular intensity data in combination with information obtained from the RD curve. Vibrational amplitudes (u_{ij}) and perpendicular correction coefficients (K_{ij}) for all 284 interatomic distances (ignoring all HH distances) were calculated by ASYM40, as described above. The geometry of the molecule was based on an r_α molecular model, which includes corrections for shrinkage effects.[18]

The final results from the experimental GED study are presented in Table 2. All major structural parameters have been refined, the only exceptions being those connected to the H atoms at the unsaturated C atoms, which were fixed at the calculated values. They make only very minor contributions to the scattering pattern. The vibrational ampli-

Table 2. Structure parameters refined in the GED study of **4** (D33). Similar data for 1,1-di-*tert*-butyl-1,3-butadiene (D11) are shown for comparison, as well as calculated (HF/6-31G*) data for both compounds. Distances (r_a) in Å, angles in degrees[a]

	4, D33 GED	HF/6-31G*		D11 GED	HF/6-31G*
C1=O4	1.221(2)	1.194	C3=C4	1.366(tied)	1.325
C2=C3	1.323(4)	1.339	C1=C2	1.380(6)	1.338
C1−C2	1.518(10)	1.482	C2−C3	1.533(22)	1.475
C3−C5	1.569(4)	1.561	C1−C5	1.557(12)	1.562
C−$CH_{3av.}$	1.530(2)	1.546	C−$CH_{3av.}$	1.551(6)	1.547
C_{sp3}−H	1.096(2)	$1.085_{av.}$	C_{sp3}−H	1.122(14)	$1.085_{av.}$
C1−C2=C3	132.6(7)	132.5	C1=C2−C3	128.2(1.6)	132.7
C2−C1=O4	116.7(9)	120.4	C2−C3=C4	121.2(2.1)	121.9
C2=C3−C5	117.9(2)	116.6	C2=C1−C5	116.1(6)	117.0
C3−C5−C6	111.7(3)	112.7	C1−C5−C6	109.5(1.0)	110.0
C2=C3C5C6	-4.8(7)	−6.8	C2=C1C5C6	−1.1(3.2)	−7.1
C2=C3C9C10	53.4(9)	54.2	C2=C1C9C10	44.2(2.1)	54.5
Vibrational amplitudes (D33)[b]					
u(C1−C2)	(ca. 1.5 Å)	0.0579(8)	0.0495		
u(C−H)	(ca. 1.1 Å)	0.0804(12)	0.0768		
u(C•H)	(ca. 2.1 Å)	0.1243(11)	0.1068		
u(C2•C5)	(ca. 2.5 Å)	0.0669(21)	0.0613		
u(C3••O4)	(ca. 3.6 Å)	0.0669(33)	0.0593		

[a] The numbering of the carbon atoms are the same in the two molecules, except for those in the conjugated system. − [b] Each of the experimental amplitudes are refined in a group together with amplitudes of similar distances.

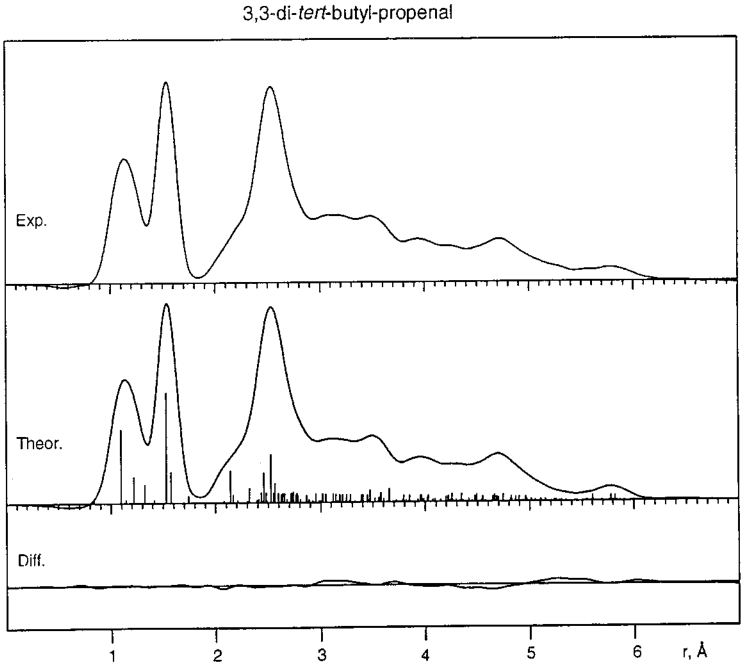


Figure 2. Experimental and theoretical RD curves for D33 (**4**) and the differences between the two curves. The CC and CO distances may be obtained from Table 3

tudes of the C−C and C−O distances, as well as those of the (O)C,H distances over one valence angle, were refined in groups.

The experimental and final theoretical molecular intensity functions are shown in Figure 1 while the corresponding radial distribution curves are presented in Figure 2. The two theoretical curves were calculated from the parameters listed in Table 2. Because of the large number of C−C and C−O distances in **4**, it is difficult to illustrate all of these in the RD curve. They may, however, be identified from Table 3, which lists the nonbonded CC/CO distances in order of increasing length. Table 3 also includes the calculated vibrational amplitudes.

Table 3. Nonbonded CC and CO distances in **4** (r_a) from the GED study and calculated vibrational amplitudes. Both quantities are given in Å. The number of dots between the atoms is equal to the number of valence angles separating them

Distance	r_a	u_{ij}	Distance	r_a	u_{ij}
C2•O4	2.318	0.0580	C2••C7	3.444	0.1238
C10•C11	2.432	0.0711	C3••O4	3.574	0.0593
C6•C8	2.452	0.0726	C2••C8	3.576	0.1109
C6•C7	2.454	0.0735	C7•••C12	3.650	0.2488
C11•C12	2.465	0.0750	C5••C12	3.658	0.1302
C2•C5	2.481	0.0613	C5••C10	3.794	0.1157
C3•C12	2.514	0.0757	C2••C11	3.851	0.0749
C3•C7	2.515	0.0781	C8•••C10	3.954	0.2223
C3•C10	2.529	0.0760	C1••C5	3.965	0.0695
C7•C8	2.534	0.0784	C6••C9	4.027	0.0754
C2•C9	2.536	0.0629	C1•••C6	4.220	0.0938
C10•C12	2.547	0.0789	O4••••C10	4.254	0.2519
C3•C6	2.562	0.0681	O4•••C9	4.346	0.0912
C3•C8	2.567	0.0774	C8•••C12	4.472	0.1163
C1•C3	2.596	0.0624	O4••••C12	4.491	0.2501
C3•C11	2.635	0.0737	C6•••C11	4.550	0.1018
C5•C9	2.723	0.0698	C7•••C10	4.646	0.1047
C2••C6	2.772	0.0823	O4••••C6	4.661	0.1290
C8•••C11	2.954	0.1464	C1•••C11	4.682	0.0971
C2••C10	3.018	0.1096	O4•••C5	4.744	0.0851
C5••C11	3.048	0.0968	C1•••C7	4.822	0.1413
C2••C12	3.119	0.1261	C6•••C12	4.863	0.1450
C1•••C10	3.143	0.1596	C6•••C10	4.896	0.1489
C1••C9	3.183	0.0935	C1•••C8	4.960	0.1184
C8••C9	3.207	0.1131	O4••••C7	5.603	0.2191
C7••C9	3.244	0.1232	O4••••C11	5.815	0.0977
C7•••C11	3.282	0.1338	O4••••C8	5.777	0.1609
C1•••C12	3.387	0.1826			

Discussion

MM3 calculations performed on all the di-*tert*-butyl-substituted 1,3-butadienes[8] have shown that the strain energy of the 1,1-disubstituted isomer is substantially larger than that of the other isomers. Because of the similarity of the 1,1-di-*tert*-butyl-1,3-butadiene and D33 structures, the strain energy of the latter compound should also be substantial.

In order to obtain some idea about the magnitude of the steric strain energy of D33, we calculated the enthalpy of

Table 4. Energies (Hartrees/molecule) corrected for zero-point vibration for the molecules appearing in Equations (1) − (3), from ab initio HF/6-31G* optimization calculations

	E(HF)	Z.p.c.[a]	E(HF) + Z.p.c.
$H_2C{=}CH{-}C{=}O$	−190.762424	0.066455	−190.695970
$E{-}CH_3CH{=}CHCH{=}O$	−229.801049	0.096262	−229.704787
$(CH_3)_2C{=}CHCH{=}O$	−268.833147	0.126086	−268.707061
$(t\mathrm{But})_2{-}C{=}CHCH{=}O$	−503.002736	0.310393	−502.692343
CH_4	−40.195172	0.047777	−40.147395
$(CH_3)_3CH$	−157.340519	0.138796	−157.201722
H_2	−1.126828	0.010591	−1.116237

[a] Zero-point energy correction.

the following reactions (1−3), on the basis of ab initio HF/6-31G* optimization calculations. Frequency calculations were carried out for all compounds involved, so that zero-point energy corrections could be accounted for. The energies are presented in Table 4.

$$H_2C{=}CH{-}CH{=}O + CH_4 \rightarrow CH_3{-}CH{=}CH{-}CH{=}O + H_2,\ \Delta H_1 = 14.1\ \text{kcal mol}^{-1} \quad (1)$$

$$H_3C{-}CH{=}CH{-}CH{=}O + CH_4 \rightarrow (CH_3)_2C{=}CH{-}CH{=}O + H_2,\ \Delta H_2 = 18.1\ \text{kcal mol}^{-1} \quad (2)$$

$$H_2C{=}CH{-}CH{=}O + 2\,(CH_3)_3CH \rightarrow (t\text{Bu})_2C{=}CH{-}CH{=}O + 2\,H_2,\ \Delta H_3 = 109.6\ \text{kcal mol}^{-1} \quad (3)$$

The value ΔH_1 may be considered as a reference energy value for replacing a hydrogen with a carbon atom in 2-propenal. The value ΔH_2 is larger than ΔH_1 because of the steric strain introduced by the two *gem* dimethyl groups. The steric strain energy of D33 is estimated to be approximately equal to $\Delta H = \Delta H_3 - \Delta H_1 - \Delta H_2 = 77.4\ \text{kcal mol}^{-1}$.

The effect of steric strain on the geometrical parameters of D33 and other, less crowded, similar molecules is illustrated by the data presented in Table 5. The data are the result of ab initio HF/6-31G* optimization calculations.

In Table 6, the experimental structure parameters of D33 are compared with those of other, less sterically crowded, conjugated enones. While the other enones are present as a mixture of *anti* and *syn* conformers, with *anti* being the most abundant, only the *anti* conformer of D33 has been identified in the present study. This is easy to explain, as the D33 *syn* conformer would clearly be additionally strained, relative to the *anti* conformer, due to repulsion between the (*Z*) *tert*-butyl and the carbonyl groups.

The steric strain due to the *gem*-di-*tert*-butyl substituents also manifests itself in the geometric parameters, especially in the C=C−C [132.6(7)°] and C−C=O [116.7(9)°] angles. The bond distances have also been affected. The C−C bond between the two unsaturated bonds has been extended, and the C=C bond appears to be shorter than that normally observed. A possible explanation for a shortening of the C=C bond might be related to the change of hybridization at C2 as a result of the opening of the C=C−C angle. The accuracy of the data, however, does not allow us do draw definite conclusions on this point.

In Table 2, the experimental and theoretical structure parameters obtained for D33 are compared to similar data obtained for D11. The main difference between the two molecules is in the unsubstituted unsaturated bonds: D33 (C=O); D11 ($C{=}CH_2$). Both molecules are found to exist in *anti* conformations, and in this form the potentially larger nonbonded repulsions involving the terminal CH_2 group of D11 are expected to be negligible.

In D11, the steric strain manifests itself in the following structural details:

- very large C=C−C angle on the substituted side,
- the (*Z*)-oriented *tert*-butyl group is twisted to a nearly staggered position relative to the C=C bond, forming a cogwheel system with the other *tert*-butyl group, which has the normal eclipsed conformation relative to the C=C bond,
- the $C(sp^2){-}C_{t\text{Bu}}$ bonds are elongated compared to those of unstrained compounds,

Table 5. Geometrical parameters from ab initio HF/6-31G* and MP2/6-31G* optimization calculations illustrating the effects of increasing internal steric strain in 2-propenal derivatives

Results from HF/6-31G* calculations (deg. and Å)	2-propenal	(*E*)-2-butenal	3-methyl-2-butenal	3,3-di-*tert*-butyl-2-propenal
C3=C2−C1	121.3	121.1	125.1	132.5
C2−C1=O	123.4	124.2	123.3	120.4
C2=C3−C(*E*)	−	125.1	119.1	116.6
C2=C3−C(*Z*)	−	−	123.4	120.7
C=C	1.321	1.324	1.331	1.339
=C−C=	1.479	1.473	1.471	1.482
C=O	1.190	1.191	1.194	1.194
C3−C(*E*)	−	1.507	1.517	1.561
C3−C(*Z*)	−	−	1.520	1.567
Results from MP2/6-31G* calculations (deg. and Å)	**2-propenal**	**(*E*)-2-butenal**	**3-methyl-2-butenal**	**3,3-di-*tert*-butyl-2-propenal[a]**
C3=C2−C1	120.5	120.6	124.7	(132.6)
C2−C1=O	124.1	124.4	123.2	(120.3)
C2=C3−C(*E*)	−	124.7	119.1	(116.8)
C2=C3−C(*Z*)	−	−	122.8	(120.0)
C=C	1.343	1.346	1.353	(1.364)
=C−C=	1.478	1.473	1.469	(1.478)
C=O	1.216	1.217	1.221	(1.223)
C3−C(*E*)	−	1.505	1.515	(1.543)
C3−C(*Z*)	−	−	1.517	(1.548)

[a] Close to energy minimum, but minimum not reached after more than 300 cpu hours.

Table 6. Experimentally obtained structure parameters for some α,β-unsaturated carbonyl compounds (distances in Å, angles in degrees)

	2-Propenal	2-Methyl-2-propenal	Methyl vinyl ketone	D33 (4)
Method:	MW	MW/GED	MW/GED/IR	GED
Ref:	[19]	[20]	[21]	present study
Dist. Type	r_s	r_g	r_g	r_g
r(C=C)	1.340(4)	1.347(3)	1.336(3)	1.325(4)
r(C=O)	1.214(4)	1.217(3)	1.219(3)	1.222(2)
r(C−C)	1.468(4)	1.487(6)	1.494(20)	1.520(10)
r(C−R)	-	1.509(6)	1.520(20)	$1.575(4)_{av}$
C=C−C	120.4(5)	118.5(5)	125.9(15)	132.6(7)
C−C=O	124.0(6)	122.9(5)	119.7(15)	116.7(9)
Conf.:	*anti* (abund.) + *syn*	89% anti + 11% *syn*	80% *anti* + 20% *syn*	100% *anti*

- the $C(sp^2)-C_{tBu}$ bonds are longer than the $C(sp^3)-CH_3$ bonds.

All the characteristics observed for D11 are also found in D33. This is of course no surprise, but in the study of D11 the discussion was to a large degree based on the theoretically obtained results, as the experimental data for D11 were of relatively poor quality. The experimental data for D33, however, are of excellent quality, and the good correspondence between the results obtained for the two molecules does, therefore, also permit more confidence in those obtained for D11. The difference in the quality of the experimental data for D33 and D11 is reflected in the standard deviations of the parameters determined for the two compounds. Even if more parameters are refined for D33 [r(C=O) and vibrational amplitudes] than for D11, the standard deviations for the latter are 2−3 times larger than those for D33. The steric strain due to gem-di-*tert*-butyl substitution is discussed in more detail in the D11 paper.[1]

Experimental Section

Spectrometers and other equipment used have already been described in previous publications in this series.[22] − Both the alcohol **2** and the chloride **3** are known compounds;[23] however, since the reported experimental details are only cursory and the spectroscopic data are largely missing, we report the syntheses of these intermediates here in full detail.

3-*tert*-Butyl-4,4-dimethyl-1-penten-3-ol (2): 2,2,4,4-Tetramethyl-3-pentanone (**1**) (70.0 g, 0.49 mol) was added at 0 °C to a solution of vinylmagnesium bromide (prepared from magnesium (35.0 g, 1.44 mol) and vinyl bromide (160.4 g, 106 mL, 1.5 mol) in 1 L of anhydrous tetrahydrofuran). After stirring for 2 h, the mixture was hydrolyzed and the organic layer was washed with a saturated aqueous solution of ammonium chloride. The aqueous phase was extracted carefully with diethyl ether, and the organic phases were combined and dried with sodium sulfate. After removal of the solvent by rotary evaporation, the remaining oil was purified by fractional distillation to provide 74.2 g (90%) of **2** as a colorless liquid, b.p. 103−105 °C/38 Torr; ref.[23] b.p. 75−80 °C/20 Torr. − ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.05 (s, 18 H, *t*Bu), 1.45 (s, 1 H, OH), 5.09−5.11 (m, 1 H, =CH), 5.13−5.14 (m, 1 H, =CH), 6.13−6.21 [m, 1 H, H(C)C=C]. − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.7 (q, C-5, C-7), 39.8 (s, C-4, C-6), 81.6 (s, C-3), 111.4 (t, C-1), 141.1 (d, C-2). − IR (film): $\tilde{\nu}$ = 3630 cm^{-1}, 1392, 1370, 1132, 980, 915. − UV (acetonitrile): λ_{max} (log ε) = 208 nm (2.47). − MS (70 eV): m/z = 168 (2) [M − 2H], 113 (30), 57 (40), 43 (100).

3-*tert*-Butyl-1-chloro-4,4-dimethyl-2-pentene (3): A solution of thionyl chloride (79.1 g, 49.1 mL, 0.66 mol) in anhydrous ether (120 mL) was added under nitrogen and with ice cooling to a solution of **2** (45.0 g, 0.26 mol) and anhydrous pyridine (40.3 g, 40.2 mL, 0.51 mol) in ether (150 mL). The reaction mixture was stirred for 2.5 h at room temp. and then carefully hydrolyzed by the addition of ice/water. The organic phase was separated and the aqueous layer was extracted several times with ether. The combined organic phases were dried with sodium sulfate, the solvent was removed in vacuo, and the remaining oil was distilled: 28.9 g (58%) of **3** as a colorless liquid, b.p. 52−54 °C/0.6 Torr, ref.[23] b.p. 90 °C/15 Torr. − ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.20 (s, 9 H, *t*Bu), 1.31 (s, 9 H, *t*Bu), 4.36 (d, 2 H, ^3J = 7.9 Hz, CH_2), 5.49 (t, 1 H, ^3J = 7.9 Hz, =CH). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.6, 33.4 (q, C-5 and C-7), 37.2, 38.7 (s, C-4 and C-6), 44.1 (t, C-1), 121.4 (d, C-2), 158.0 (s, C-3). − IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 1392, 1368, 670. − UV (acetonitrile): λ_{max} (log ε) = 204 nm (3.89). − MS (70 ev) m/z (%) = 152 (2) [M^+ − Cl], 96 (72), 81 (56), 57 (100).

3-*tert*-Butyl-4,4-dimethyl-2-pentenal (4): Freshly distilled 2-nitropropane (72.7 g, 73.3 mL, 0.82 mol) was added at room temp. to a solution of potassium hydroxide (30.9 g, 0.55 mol) in water (70 mL) and 2-propanol (230 mL).[24] After the mixture had been stirred for 30 min, a solution of **3** (38.0 g, 0.20 mol) in 2-propanol (80 mL) was added at room temp., and the reaction mixture was heated under reflux for 6.5 h. After hydrolytic workup, the aqueous phase was extracted several times with ether, and the organic phases were combined and dried with sodium sulfate. The solvent was removed in vacuo and the remaining oily residue was distilled to afford 22.5 g (66%) of **4** as a colorless liquid, b.p. 65 °C/0.5 Torr. − ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.28 (s, 9 H, *t*Bu), 1.49 (s, 9 H, *t*Bu), 5.96 (d, 1 H, ^3J = 7.4 Hz, =CH), 10.50 (d, 1 H, ^3J = 7.4 Hz, CHO). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.0, 35.3 (q, C-5 and C-7), 39.2, 39.7 (s, C-4 and C-6), 126.6 (d, C-2), 178.0 (s, C-3), 193.8 (d, C-1). − IR (film): $\tilde{\nu}$ = 2963 cm^{-1}, 1733, 1393, 1368, 1152. − UV (acetonitrile): λ_{max} (log ε) = 246 nm (3.62) − MS (70 eV): m/z (%) = 167 (38) [M^+ − H], 127 (20), 57 (100). − $C_{11}H_{20}O$ (168.3); calcd. C 78.51, H 11.98; found C 78.32, H 11.85.

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