

Stereoelectronic Structure of α -Bromoalkenyl Trifluoromethyl Ketones

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Received December 14, 2008

Abstract—The results of quantum-chemical calculations at the B3LYP/6-311G** level of theory showed that (*Z*)- α -bromo- β -arylalkenyl trifluoromethyl ketones are more stable than the corresponding *E* isomers by 4–5 kcal/mol. Relatively large positive charge on the olefinic β -carbon atom and strong polarization of the C=C bond in both *Z-s-cis* and *Z-s-trans* conformers makes bromoalkenyl trifluoromethyl ketones the most potent Michael acceptors among α,β -unsaturated carbonyl compounds. The calculated data are very consistent with the experimental IR spectra.

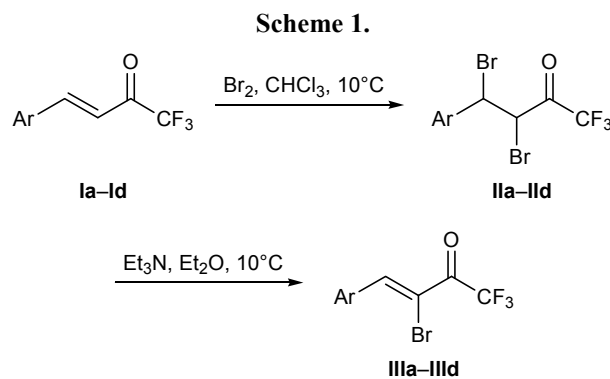
DOI: 10.1134/S1070428009100017

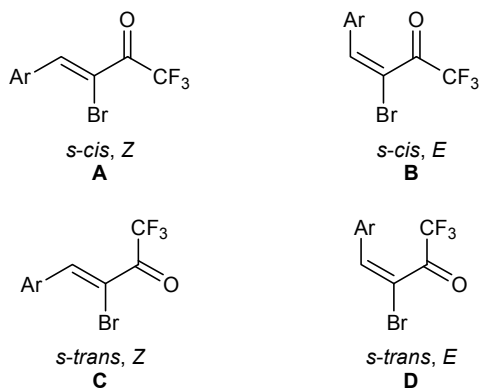
Unsaturated carbonyl compounds play an important role in synthetic organic chemistry and attract interest as model structures for theoretical studies. α -Halo derivatives of α,β -unsaturated carbonyl compounds exhibit a high reactivity toward nucleophilic reagents and are convenient models for studying transmission of electronic effects through the C=C(H)gC=O conjugated system [1, 2]. It is known that introduction of a fluorine atom or fluorine-containing group into organic molecules considerably changes their physical and chemical properties. It is not accidental that the chemistry of unsaturated trifluoromethyl ketones has developed extensively during the past decades, and these compounds have been widely used in the synthesis of acyclic and carbo- and heterocyclic compounds [3–6]. Polyfunctionality and accessibility of haloalkenyl trifluoromethyl ketones makes them undoubtedly advantageous as intermediate products for the preparation of various biologically active substances and analogs of natural compounds. For example, we recently reported on unexpected one-pot transformation of 4-aryl-3-bromo-1,1,1-trifluoromethylbut-3-en-2-ones into indenols by the action of secondary amines [7, 8].

With a view to understand specific reactivity of alkenyl trifluoromethyl ketones having a halogen atom in the α -position, it is necessary to thoroughly analyze their structure and the nature of electronic interactions in their molecules. In the present work we examined

the stereoelectronic structure of α -haloalkenyl trifluoromethyl ketones in comparison with their non-fluorinated analogs on the basis of the results of DFT quantum-chemical calculations (B3LYP/6-311G**) and IR spectral data.

α -Bromo enones **IIIa–IIIId** were synthesized according to a classical procedure implying bromination of initial enones **Ia–Id** and subsequent dehydrobromination of dibromo derivatives **IIa–IIId** thus obtained [7, 8] (Scheme 1). α -Haloalkenyl trifluoromethyl ketones are typical captodative alkenes, which can exist as several stereoisomers **A–D** arising from *cis–trans* isomerism about the C=C bond and rotation of the trifluoroacetyl group about the C–C bond. According to the ^1H and ^{13}C NMR data, α -bromo enones





IIIa–III d have *Z* configuration with respect to the C=C bond with *s-cis* orientation with respect to the single C–C bond in the C=C–C=O fragment [8].

The IR spectra of enones **IIIa–III d** recorded from thin film (**IIIa**) or KBr pellets (**IIIb–III d**) contain strong absorption bands with approximately equal intensities due to stretching vibrations of the C=O and C=C bonds, indicating *s-cis* orientation of these groups [9, 10]. In the spectrum of **IIIa**, the $\nu(\text{C=O})$ and $\nu(\text{C=C})$ bands appear at 1714 and 1593 cm^{-1} , respectively, for the neat substance, and they shift to 1716 and 1595 cm^{-1} and to 1721 and 1596 cm^{-1} in going to CDCl_3 and CCl_4 , respectively. However, the intensity ratio of these bands remains unchanged, which may be regarded as an additional support to *s-cis* conformation of the *Z* isomer of **IIIa** in inert medium. In the IR spectra of both liquid and crystalline bromo enone **Z-IV** and bromo enal **Z-V** having no electron-withdrawing CF_3 group in their molecules, the $\nu(\text{C=O})$ band is displaced toward lower frequencies by $\sim 30 \text{ cm}^{-1}$, as compared to enone **IIIa**, while the $\nu(\text{C=C})$ band has a higher frequency but by no more than 10 cm^{-1} (Table 1). As in the spectra of **IIIa**, the intensity ratio corresponds to the *s-cis* conformer. On the other hand, the intensity of the carbonyl absorption band in the IR spectra of solutions of **IV** and **V** in CDCl_3 (1685 and 1697 cm^{-1} , respectively) is higher than the intensity of the $\nu(\text{C=C})$ band ($\sim 1600 \text{ cm}^{-1}$). The difference in the absorption intensities increases in going to weakly polar carbon tetrachloride. The $\nu(\text{C=O})$ bands of **IV** and **V** in this solvent (1692 and 1705 cm^{-1} , respectively) are very strong, whereas the $\nu(\text{C=C})$ bands have medium intensity. This means that, unlike α -bromoalkenyl trifluoromethyl ketones **Z-III**, compounds **Z-IV** and **Z-V** in inert medium exist as equilibrium mixtures of *s-trans* and *s-cis* conformers. Increase of solvent polarity shifts the equilibrium toward *s-trans* conformer.

Quantum-chemical calculations performed for isolated molecules showed that the *Z* isomers of **IIIa** (*s-trans* or *s-cis*; heavy atoms constituting the π -electron system lie in one plane) are more stable than the corresponding *E* isomers by 4–5 kcal/mol (Table 2). The reason is that the C=C double bond in the *E*-isomers is forced out from both aromatic ring plane (by $\sim 30^\circ$) and carbonyl group plane (by 53 and 43° for the *s-trans* and *s-cis* conformers, respectively). The difference in the energies of formation of the *s-trans* and *s-cis* conformers of *E-IIIa* does not exceed 0.5 kcal/mol, whereas the *s-trans-Z* structure of **IIIa** is more stable than *s-cis-Z* by 1.48 kcal/mol. According to the MP2/6-311G** calculations, the *s-trans* conformer is also more stable, but the energy difference is $\Delta E = 1.82 \text{ kcal/mol}$. Taking into account small difference in the dipole moments of the *s-trans* and *s-cis* conformers ($\mu = 5.09$ and 4.80 D, respectively), we cannot assume stabilizing effect of solvent polarity. Stabilization of the less polar *s-cis* conformer of **Z-V** ($\mu = 3.08 \text{ D}$) in the solid state may be determined by specificity of its crystal packing. While studying α -bromo- β -aminoalkenyl trifluoromethyl ketones [11] we already observed stabilization of the corresponding *s-cis* conformers despite lower energy of *s-trans* conformers (by 1.4–1.8 kcal/mol). Almost similar energy differences between the conformers were obtained by calculations at the B3LYP/6-31G**, PBE/QZ3P, and riMP2/cc-pVTZm levels of theory.

Nucleophilic 1,4-addition reactions are typical transformations of α,β -unsaturated carbonyl compounds. Therefore, in order to evaluate general reactivity of α -bromoalkenyl trifluoromethyl ketones we examined the effects of their conformation and nature of substituent in the benzene ring on the polarizability of the C=C bond in the conjugated system C=C–C=O. For this purpose, we defined the polarity of the double $\text{C}^\alpha=\text{C}^\beta$ bond (Δq) as the difference in the charges on the C^α and C^β atoms. The latter were calculated for the *Z* isomers of a series of enones with *s-trans* and *s-cis* orientations of the C=C and C=O bonds and different substituents in the benzene ring, as well as for the *s-trans* and *s-cis* conformers of a series of α -substituted enones and enals (Table 1).

The results showed that the *s-trans* conformers of unsaturated trifluoromethyl ketones **IIIa–III e** and **VI** are energetically more favorable than their *s-cis* structures by 1.3–1.8 kcal/mol (Table 1). The *s-trans* conformers of acrolein (**VII**) and its homologs both in the gas phase and in inert solvents are also more stable [9].

Table 1. Calculated (B3LYP/6-311G**) parameters of *s-trans* and *s-cis* conformers of substituted enones **Ia**, **IV**, **VI**, and **X–XII**, enals **V** and **VII–IX**, and *Z* isomers of α -bromoalkenyl trifluoromethyl ketones **IIIa–IIIe**

Comp. no.	R	X	Y	C=C–C=O (<i>s-trans</i>)						C=C–C=O (<i>s-cis</i>)					
				ΔE^a	q^b	Δq^c		$\nu(\text{C=C})^d$	$\nu(\text{C=O})^d$	ΔE	q	Δq		$\nu(\text{C=C})$	$\nu(\text{C=O})$
					C^β	C=C	C=O				C^β	C=C	C=O		
Ia	Ph	H	CF ₃	1.27	–0.020	0.136	0.377	1672	1767	0	0.001	0.181	0.379	1658	1786
IIIa	Ph	Br	CF ₃	0	0.036	0.321	0.432	1630	1782	1.48	0.058	0.328	0.410	1602 (1593) ^e	1771 (1714) ^e
IIIb	4-MeOC ₆ H ₄	Br	CF ₃	0	0.041	0.332	0.439	1626	1775	1.39	0.061	0.337	0.416	1599 (1585) ^f	1761 (1692) ^f
IIIc	2,5-(MeO) ₂ -C ₆ H ₃	Br	CF ₃	0	0.068	0.344	0.433	1627	1779	1.80	0.098	0.365	0.408	1600 (1570) ^f	1767 (1695) ^f
IIId	2-Thienyl	Br	CF ₃	0	0.081	0.373	0.435	1632	1776	1.28	0.099	0.377	0.414	1606 (1580) ^f	1762 (1700) ^f
IIIe	4-O ₂ NC ₆ H ₄	Br	CF ₃	0	0.037	0.319	0.422	1630	1792	1.33	0.058	0.324	0.400	1614	1781
IV	Ph	Br	CH ₃	1.81	0.016	0.297	0.545	1650	1765	0	0.055	0.341	0.552	1626 (1603) ^e	1757 (1685) ^e
V	Ph	Br	H	0.31	0.023	0.287	0.513	1650	1788	0	0.059	0.367	0.528	1628 (1602) ^f	1774 (1681) ^f
VI	H	Br	CF ₃	0	–0.075	0.196	0.406	1652	1809	1.81	–0.061	0.197	0.397	1633	1800
VII	H	H	H	0	–0.168	0.001	0.472	1680 (1618) ^e	1786 (1704) ^e	1.67	–0.129	0.083	0.472	1666	1790
VIII	H	Br	H	0	–0.107	0.151	0.495	1656	1805	0.13	–0.072	0.211	0.510	1648	1793
IX	H	Cl	H	0.01	–0.090	0.168	0.515	1663 (1610) ^e	1806 (1730) ^e	0	–0.054	0.233	0.531	1657	1798
X	H	H	Me	0.41	–0.169	0.012	0.490	1683 (1618) ^e	1761 (1685) ^e	0	–0.127	0.074	0.506	1670 (1618) ^e	1780 (1706) ^e
XI	H	H	CF ₃	0.83	–0.139	0.021	0.364	1680	1792	0	–0.115	0.070	0.376	1672	1809
XII	H	Br	Me	1.16	–0.107	0.149	0.521	1656	1783	0	–0.071	0.195	0.536	1643 (1609) ^e	1776 (1697) ^e

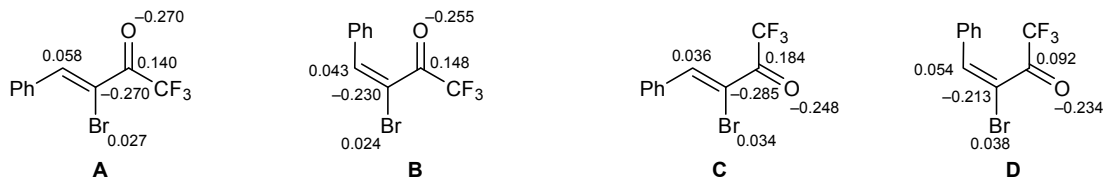
^a Difference in the total energies of formation, kcal/mol.^b Charge on atom, *e*.^c Difference in the charges on atoms, *e*.^d Calculated stretching vibration frequency, cm^{–1}.^e Experimental frequency (neat).^f Experimental frequency (KBr).

The difference in the energies of formation of the above conformers sharply decreases ($\Delta E = 0.4$ – 0.01 kcal/mol) in going to α -haloacroleins **VIII** and **IX**, bromo enone **V**, and unsubstituted enone **X**. The *s-cis* conformer turned out to be more stable for compounds **Ia**, **IV**, **XI**, and **XII** ($\Delta E \leq 1.81$ kcal/mol).

Both conformers of **Ia** and **VI–XII** are characterized by a negative charge on C^β and low polarity of the double C=C bond. The negative charge on C^β in the *s-cis* conformers is smaller, while the C=C bond is more polar than in the corresponding *s-trans* con-

formers. The polarities of the C=O group in different conformers of **Ia** and **VI–XII** differ insignificantly, and molecules having no bromine atom possess considerably less polar C=O bond.

The presence of phenyl and trifluoromethyl groups in bromo enones **III** makes the C=C bond more polar, and the difference in the polarities of that bond in the *s-trans* and *s-cis* conformers is small. In addition, the C^β atom bears a positive charge which is considerably larger in the *s-cis* conformers (Table 1). Unsubstituted trifluoromethyl ketone **Ia** is characterized by lower

Table 2. Charge distribution (q , e) in different stereoisomers of 3-bromo-1,1,1-trifluoro-4-phenylbut-3-en-2-one (**IIIa**), calculated by the B3LYP/6-311G** method

Parameter	A (<i>Z, s-cis</i>)	B (<i>E, s-cis</i>)	C (<i>Z, s-trans</i>)	D (<i>E, s-trans</i>)
ΔE^a	1.48	5.02	0	5.57
μ^b	4.80	5.09	5.09	4.10
Δq^c	0.328	0.273	0.321	0.267

^a Difference in the total energies of formation, kcal/mol.

^b Dipole moment, D.

^c Polarity of the C=C bond, e .

positive charge on C^β and less polar C=C bond. Introduction of an electron-withdrawing substituent (e.g., nitro group) into the benzene ring (**IIIe**) weakly affects the above parameters, whereas electron-donating groups (e.g., MeO in **IIIb**) favor increased positive charge on C^β and higher polarity of the C=C bond. The strongest effect was observed for compounds **IIIc** and **IIId** having a 2,5-dimethoxyphenyl or thienyl group, respectively, on the β-carbon atom, especially for their *s-cis* conformers. The polarity of the carbonyl group is weakly sensitive to the substituent nature and conformation. Compounds **IV** and **V** having no trifluoromethyl group occupy an intermediate place. The positive charge on C^β and polarization of the C=C bond in the *s-cis* conformers of **IV** and **V** approach the corresponding values for α-bromoalkenyl trifluoromethyl ketones **IIIa–IIIe** but considerably exceed those found for the *s-trans* conformers of **IV** and **V**. Thus, unlike nonfluorinated analogs, bromoalkenyl trifluoromethyl ketones **IIIa–IIIe** are characterized by fairly large positive charge on the β-carbon atom at the double bond and stronger polarization of that bond. This means that bromoalkenyl trifluoromethyl ketones **III** should behave as the most reactive Michael acceptors among α,β-unsaturated carbonyl compounds.

We also calculated normal vibration frequencies of the compounds under study in *s-trans* and *s-cis* conformations with a view to compare the calculated values with the IR spectral data and electron density distribution in their molecules (Table 1). The calculated ν(C=O) frequencies for the *s-cis* conformers of unsubstituted acrolein (**VII**), methyl vinyl ketone (**X**), trifluoromethyl vinyl ketone (**XI**), and enone **Ia** are

higher than those found for their *s-trans* conformers, which may be due to weaker conjugation in the *s-cis* structure. These data are very consistent with the IR spectra of enones [9]. However, introduction of a halogen atom into the α-position leads to a considerably different pattern. The ν(C=O) and ν(C=C) frequencies calculated for the *s-trans* conformers of *Z*-**IIIa** and *E*-**IIIa** are higher than for their *s-cis* conformers. The same applies to other α-halo-substituted unsaturated carbonyl compounds: the difference in the ν(C=O) frequencies is 10–20 cm⁻¹. The lower ν(C=C) frequency for the *s-cis* conformers of all the examined α-halo derivatives corresponds to increased polarization of the C=C bond therein.

The calculated ν(C=O) frequencies of the *s-trans* conformers of α-halo-substituted acroleins **VIII** and **IX** are higher, while the ν(C=C) frequencies are lower by ~20 cm⁻¹, than those of more stable *s-trans* conformer of acrolein (**VII**). These data are consistent with variation of the corresponding frequencies in the IR spectra of α-chloroacrolein (1730 and 1610 cm⁻¹) [12] as compared to acrolein (1704 and 1618 cm⁻¹) [9], which exist in solution preferentially as *s-trans* conformers. α-Bromovinyl methyl ketone (**XII**) and bromine-free analog **X** displayed similar variations of the calculated ν(C=O) and ν(C=C) frequencies of the *s-trans* conformers and reduction of ν(C=C) of the *s-cis* conformers, the ν(C=O) frequency remaining almost unchanged. This is reflected in the ν(C=O) values in the IR spectra of enone **X** which exists as *s-trans* and *s-cis* conformers (1685 and 1706 cm⁻¹) [9] and bromo enone **XII** in the *s-cis* conformation (1697 cm⁻¹). In addition, the ν(C=C) frequency of

compound **XII** decreases to 1609 cm^{-1} relative to $\nu(\text{C}=\text{C})$ of enone **X** (1618 cm^{-1}). Thus introduction of a bromine atom into the α -position of α,β -unsaturated carbonyl compounds reduces the negative charge on the β -carbon atom, increases polarization of the $\text{C}=\text{C}$ bond, and decreases its stretching vibration frequency.

Replacement of the methyl group in enone **IV** by trifluoromethyl (compound **IIIa**) or introduction of a halogen atom (compounds **VI–XII**) results in lower calculated $\nu(\text{C}=\text{C})$ frequencies and increased $\nu(\text{C}=\text{O})$ values. In the IR spectrum of enone **IIIa** the corresponding absorption maxima are displaced to 1593 and 1714 cm^{-1} relative to analogous bands in the spectrum of **IV** (1603 and 1685 cm^{-1}).

According to the calculations, stretching vibrations of the $\text{C}=\text{C}$ bond in bromo enones **III** are strongly overlapped by vibrations of the aromatic ring, and introduction of an electron-withdrawing substituent into the benzene ring weakly affects the calculated $\nu(\text{C}=\text{C})$ frequency, although this leads to considerable polarization of the double bond in the *s-cis* conformers. Nevertheless, increased polarization of the $\text{C}=\text{C}$ bond is accompanied by reduction of the $\nu(\text{C}=\text{C})$ frequency in the IR spectra of enones **IIIb** and **IIIc** by $10\text{--}20\text{ cm}^{-1}$ as compared to enone **IIIa** having no substituent in the benzene ring. Considerable increase in the positive charge on the β -carbon atom and in the polarity of the $\text{C}=\text{C}$ bond in bromo enone **IIIb** corresponds to both reduction in the calculated $\nu(\text{C}=\text{C})$ frequency and low-frequency shift of the $\nu(\text{C}=\text{C})$ band in the IR spectrum. The calculated $\nu(\text{C}=\text{O})$ frequency decreases by 10 and 4 cm^{-1} upon introduction of one (**IIIb**) or two (**IIIc**) methoxy groups, respectively. In the IR spectra of these compounds, the low-frequency shift of the $\nu(\text{C}=\text{C})$ band reaches $\sim 20\text{ cm}^{-1}$. Insofar as the polarity of the $\text{C}=\text{O}$ bond remains almost unchanged, reduction of the $\nu(\text{C}=\text{O})$ frequency is largely determined by variation of geometric parameters of that bond, i.e., its length and CCO bond angle, rather than by electronic effect of substituents, which is typical of carbonyl-containing compounds [10]. The same applies to the reduced $\nu(\text{C}=\text{O})$ frequency for *s-cis* conformers of bromo enones with simultaneous decrease in the $\text{C}=\text{O}$ bond polarization.

Thus the *s-cis* conformers of α -bromoalkenyl trifluoromethyl ketones **Z-III** possess a strongly polarized $\text{C}=\text{C}$ bond. As a result, its stretching vibration frequency decreases, and the difference in the calculated $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ frequencies increases ($160\text{--}170\text{ cm}^{-1}$ against $120\text{--}150\text{ cm}^{-1}$ for other compounds

of this series). The corresponding differences in the experimental IR spectra range from 110 to 120 and from 70 to 90 cm^{-1} , respectively.

EXPERIMENTAL

Enones **IIIa–IIIb** were synthesized according to the procedure described in [8]. Enone **IV** was prepared by successive bromination–dehydrobromination of benzylideneacetone as described in [13]. α -Bromocinnamaldehyde (**V**) was synthesized according to [14]. The IR spectra were recorded from neat substances (films), KBr pellets, and solutions in CCl_4 and CDCl_3 on a Varian 3100 FT-IR spectrometer. Quantum-chemical calculations, including calculations of vibration frequencies, were performed in terms of the density functional theory (B3LYP/6-311G**) with complete geometry optimization using Gaussian 03 software package [15]. The total energies of formation were determined with correction for zero-point vibration energy.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 08-03-00067-a).

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