April, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 981—986 (1976) 981

Rotational Isomerism in β-Diketone *cis* and *trans* Enol Ethers. An IR and PMR Study*

Janusz Dabrowski** and Michal Tenger

Institute of Organic Chemistry, Polish Academy of Sciences, 00-961 Warsaw, Poland

(Received March 31, 1975)

The *cis* (*Z*) isomers of β-alkoxy-α,β-unsaturated ketones, $R^1COCH=CR^2OR^3$, have been shown by IR spectra to exist as a mixture of *s-cis* (*ZZ*) and *s-trans* (*ZE*) rotamers, with the equilibrium shifting towards the former upon increasing the steric requirements of the R^1 substituent. The *trans* (*E*) isomers have uniformly the *s-cis* (*EZ*) structure. *O-s-trans* (or non-planar) and *O-s-cis* conformations due to rotation around the C_{sp^2}–O bond have been proposed for the *Z* and *E* isomers, respectively. Based on known structures, a rationalization of the rule governing the chemical shifts of R^1 and R^2 protons, called here the "ene-one cross shielding rule", has been offered.

While the vast majority of β-keto enols obtained to date have a *cis* configuration, obviously due to the stabilizing effect of the chelate hydrogen bond, most β-keto enol ethers have the alkoxy group in the *trans* position with respect to the carbonyl. Such was *e.g.*, the case with ethers of β-keto aldehydes studied in our previous work.[1] The *cis* β-keto enol ethers are kinetic products which spontaneously isomerize into the thermodynamically stable *trans* form. With β-diketone enol ethers, the isomerization is slow enough to enable the isolation and spectral investigation of these two isomers.

The simplest representatives of this class of compounds *viz.*, *cis* and *trans* methyl ethers of the enol of acetylacetone first obtained by Eistert *et al.*[2] have recently been investigated by Awang[3] using NMR spectroscopy. Although his assignments based on indirect data (NOE and ASIS) correctly ascribed the *trans-s-cis* structure to the isomer with a lower boiling point, the *cis* isomer was erroneously assumed to be homogeneous with respect to conformation; as shown below (see Results and Discussion section and Fig. 1) a considerable amount of the *s-cis* rotamer can directly be observed in the infrared spectra together with the *s-trans* one assigned by Awang.[3] Taking advantage of the more favorable time scale of the infrared spectroscopy we have investigated here some of the factors affecting the conformational equilibria, *viz.*, the steric requirements of the alkyl substituents and the solvent effect in a series of β-diketone enol ethers.***

While the *trans*(*E*) β-keto aldehyde enol ethers exhibited up to eight IR bands in the double bond stretching region due to rotation about both the C_{sp^2}–C_{sp^2} and C_{sp^2}–O single bonds,[1] the number of bands never exceeded four in the case of the *cis(Z)* and *trans(E)* β-diketone enol ethers reported here, which indicates that some of the rotamers are not present. The scrutiny of the IR spectra permitted us to identify the existing rotamers and to estimate their populations.

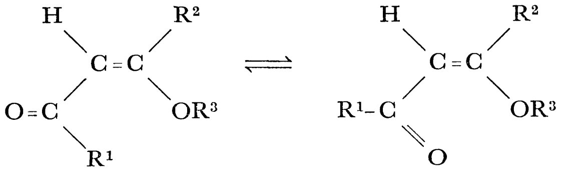
Joint utilization of the IR and NMR data allowed us to investigate the applicability of the rule[3,5–7] governing the shielding of the allylic and acylic protons in the compounds of the type studied here and to propose a rationalization of this rule.

Results and Discussion

IR Spectra. IR spectra data are given in Table 1. In order to illustrate the relationship between band intensities and steric requirements of the alkyl substituents, spectra of selected compounds are shown in Figs. 1 and 3. The dependence of the rotational equilibria upon the polarity of the solvent is illustrated by the spectra presented in Fig. 2.

In the *cis(Z)* series of β-diketone enol ethers, four bands are observed in most cases between 1550 and 1700 cm^{-1}. As seen from Fig. 1, one band in the $\nu_{C=O}$ region (band B) and one in the $\nu_{C=C}$ region (band C) decrease in intensity with increasing bulkiness of the substituent R^1 in going from compound **1** *Z* to **2** *Z*, **3** *Z* and **8** *Z*, while the other $\nu_{C=O}$ band (A) and $\nu_{C=C}$ band (D) increase in the same sequence.****

Since the enlargement of the alkyl group R^1 causes a stronger interaction with the alkoxy group in the *s-trans* conformation, these dramatic spectral changes can safely be interpreted as a result of the equilibrium shift towards the *s-cis* form:



I II

ZE (*i.e.*, *cis*/*s-trans*) *ZZ* (*i.e.*, *cis*/*s-cis*)

Consequently, as with β-keto aldehyde enol ethers[1] and other α,β-unsaturated ketones,[8,9] the "inner" bands B and C are assigned to the coupled $\nu_{C=O}$ and $\nu_{C=C}$ vibrations of the *s-trans* rotamer and the "outer" ones A and D to the same vibrations of the *s-cis* rotamer.

In view of the strong non-bonded interaction between R^1 and OR^3 it might seem surprising, at first, that the *s-trans* rotamer prevails in the case of the first homologue of the series (**1** *Z*; R^1=Me) and occurs in still

---

* Paper XX of the series, "Infrared spectra and structure of substituted unsaturated carbonyl compounds."

** Present addres: Max-Plank-Institute for Medical Research, Jahnstrasse 29, D-6900 Heidelberg, Germany.

*** Some of the compounds investigated here have been examined IR-spectroscopically by Giza,[4] but poor resolution of the spectra and some uncertainty (and even incorrectness; see footnote of Table 3) of the configurational assignments render those results unreliable.

**** Although the vibrations of the C=O and C=C groups are undoubtedly strongly coupled, the bands will be denoted, for the sake of simplicity, $\nu_{C=O}$ and $\nu_{C=C}$.

Table 1. Wave numbers (cm^{-1}) of absorption bands and probable conformational preferences of *cis* (*Z*) and *trans* (*E*) α, β-unsaturated β-alkoxy ketones, R^{1}COCH=CR^{2}OR^3 in tetrachloroethylene

Compound	R_1	R_2	R_3	Configuration	Concentration (mol/l)	Absorption bands[a] $\nu_{C=O}$		$\nu_{C=C}$		Preferred conformation	
						s-cis A	*s-trans* B	*s-trans* C	*s-cis* D	C_{sp^2}-C_{sp^2}	C_{sp^2}-O
1*Z*	CH_3	CH_3	CH_3	*cis*	0.17	1685	1660	1632	1599	*s-trans*>*s-cis*	*O-s-trans*[b]
1*E*				*trans*	0.09	1689			1590	*s-cis*	*O-s-cis*
2*Z*	CH_3CH_2	CH_3CH_2	CH_3	*cis*	0.16	1684	1659	1631	1598	*s-trans*∼*s-cis*	*O-s-trans*[b]
2*E*				*trans*	0.08	1688			1592	*s-cis*	*O-s-cis*
3*Z*	$(CH_3)_2CH$	$(CH_3)_2CH$	CH_3	*cis*	0.13	1684	1658	1627	1596	*s-cis*>*s-trans*	*O-s-trans*[b]
3*E*				*trans*	0.10	1684			1587	*s-cis*	*O-s-cis*
4*Z*	CH_3	CH_3	CH_3CH_2	*cis*	0.19	1683	1657	1630	1608	*s-trans*>*s-cis*	*O-s-trans*[b]
4*E*				*trans*	0.10	1688			1588	*s-cis*	*O-s-cis*
5*Z*	CH_3CH_2	CH_3CH_2	CH_3CH_2	*cis*	0.16	1683	1658	1630	1593	*s-trans*∼*s-cis*	*O-s-trans*[b]
5*E*				*trans*	0.09	1686			1587	*s-cis*	*O-s-cis*
6*Z*	$(CH_3)_2CH$	$(CH_3)_2CH$	CH_3CH_2	*cis*	0.15	1683	1658	1628	1589	*s-cis*>*s-trans*	*O-s-trans*[b]
6*E*				*trans*	0.11	1683			1584	*s-cis*	*O-s-cis*
7*Z*	CH_3	CH_3	$(CH_3)_2CHCH_2$	*cis*	0.18	1683	1655	1629	1600	*s-trans*>*s-cis*	*O-s-trans*[b]
7*E*				*trans*	0.12	1687			1587	*s-cis*	*O-s-cis*
8*Z*	$(CH_3)_3C$	CH_3	CH_3	*cis*	0.19	1677			1601	*s-cis*	*O-s-trans*[b]
8*E*				*trans*	0.19	1682			1592	*s-cis*	*O-s-cis*

a) The spectra of all solutions were obtained in a standard cell of thickness 0.1 mm. b) Or non-planar.

Table 2. PMR chemical shifts of *cis* (*Z*) and *trans* (*E*) β-diketone enol ethers (ppm; in CCl$_4$)

Compound[a]	Acylic protons of R^1 $-\underline{C}$-C=O	$\Delta\delta^E_Z(R^1)$	Allylic protons of R^2 $-\underline{C}$-C=C	$\Delta\delta^E_Z(R^2)$	$\Delta\delta^{R^2}_{R^1}$	Vinylic protons $\underline{H}$-C=C	$\Delta\delta^E_Z$	Ether proton (R^3) $-\underline{C}$-O-	$\Delta\delta^E_Z(R^3)$	Other signals
1*Z*	2.14	−0.10	2.02	+0.17	−0.12	4.98	+0.49	3.82	−0.19	—
1*E*	2.04		2.19		+0.15	5.47		3.63		—
2*Z*	2.53(q)	−0.15	2.31(q)	+0.42	−0.12	5.06	+0.30	3.84	−0.16	0.99(t); 1.13(t)
2*E*	2.38(q)		2.73(q)		+0.35	5.36		3.68		1.03(t); 1.06(t)
3*Z*	2.58(spt)	−0.09	2.35(spt)	+1.64	−0.13	5.23	+0.04	3.80	−0.15	1.02(d); 1.09(d)
3*E*	2.49(spt)		3.99(spt)		+1.50	5.27		3.65		1.00(d); 1.02(d)
4*Z*	2.17	−0.14	2.00	+0.20	−0.17	4.98	+0.48	4.11(q)	−0.25	1.35(t)
4*E*	2.03		2.20		+0.17	5.46		3.86(q)		1.33(t)
5*Z*	2.52(q)	−0.19	2.27(q)	+0.40	−0.15	4.99	+0.27	4.04(q)	−0.22	0.96(t); 1.10(t); 1.30(t)
5*E*	2.33(q)		2.67(q)		+0.34	5.26		3.82(q)		1.04(t); 1.08(t); 1.35(t)
6*Z*	2.57(spt)	−0.13	2.34(spt)	+1.56	−0.23	5.20	+0.01	4.04(q)	−0.24	1.06(d); 1.13(d); 1.29(t)
6*E*	2.44(spt)		3.90(spt)		+1.46	5.21		3.80(q)		1.05(d)[b]; 1.05(d)[b]; 1.35(t)
7*Z*	2.21	−0.19	2.03	+0.19	−0.17	4.90	+0.50	3.81(d)	−0.29	1.05(d) ∼2.1 multiplet[c]
7*E*	2.02		2.22		+0.20	5.40		3.52(d)		0.97(d) ∼2.1 multiplet[c]
8*Z*	—	—	1.92	+0.28	—	5.36	+0.24	3.76	−0.13	1.05
8*E*	—		2.20		—	5.60		3.63		1.10

a) See Table 1. b) Two doublets completely overlapped. c) Position difficult to determine because of strong overlap with other signals.

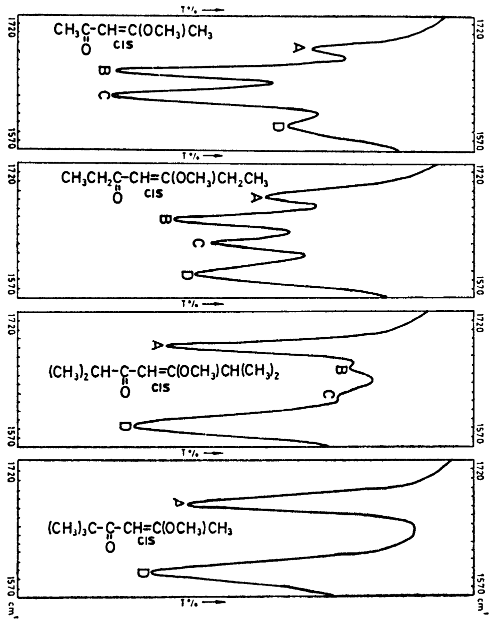


Fig. 1. Infrared spectra of compounds **1** *Z*, **2** *Z*, **3** *Z*, and **8** *Z* in tetrachloroethylene. Cell thicknesses and concentrations are given in Table 1.

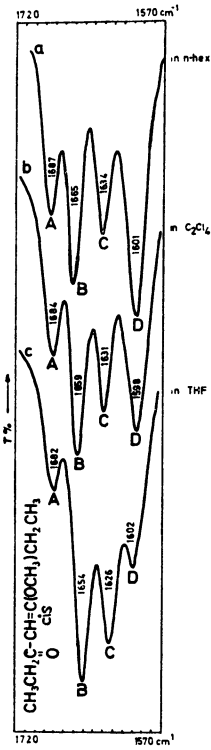


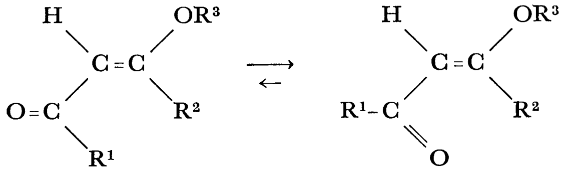
Fig. 2. Infrared spectra of compound **2** *Z*.
a in hexane;
b in tetrachloroethylene;
c in tetrahydrofuran.
Concentrations 0.16 M, cell thicknesses 0.1 mm.

considerable amounts with compound **2** *Z* (R^1=Et). This situation is in contrast with what was found for other *cis* β-substituted unsaturated ketones,[8,9] including the *trans(E)* isomers of the compounds just discussed (*vide infra*) which bear an alkyl *cis* β-substituent and exist entirely as *s-cis* rotamers. This seeming contradiction can reasonably be explained by taking into account the electrostatic repulsion between two oxygen atoms in the alternative *s-cis* conformation. The latter effect, assisted by the greater resonance energy of the *s-trans* structure, seems to account for the preponderance of the *s-trans* rotamer if R^1=Me. Now, both the electrostatic and the resonance factors are practically constant in the whole series under consideration, whereas the non-bonded R^1–OR^3 interactions in the *s-trans* rotamer obviously increase in the sequence, thus satisfactorily explaining the observed equilibrium shift.

The conformational equilibrium is apparently not affected by the size of the substituent R^3: the spectra of compounds **4** *Z*, **5** *Z*, and **6** *Z* with R^3=Et are very similar to those of **1** *Z*, **2** *Z*, and **3** *Z*, respectively, and substitution of R^3=Me by *i*-Bu (compound **7** *Z*) has practically no effect on the relative intensities of the IR bands A—D.

The solvent-induced intensity changes are in agreement with the assignments of the two $\nu_{C=O}$ and two $\nu_{C=C}$ bands: when passing from hexane to tetrachloroethylene and particularly to the considerably more polar tetrahydrofuran solutions, an increase of bands B and C of the more polar *s-trans* form at the expense of the bands A and D is observed (*e.g.*, with R^1=Et a reversal of band intensities occurs; see for **2** *Z* in Fig. 2).

With the *trans(E)* series, only one $\nu_{C=O}$ and one $\nu_{C=C}$ band are observed; their positions clearly indicate that the only observed rotamer is the *s-cis* one (see Fig. 3). This decisive equilibrium shift is obviously due to steric interactions between the R^1 and R^2 alkyl groups in the *s-trans* form:



III IV

EE (*i.e.*, *trans/s-trans*) *EZ* (*i.e.*, *trans/s-cis*)

It must be noted, however, that in some of the *trans* compounds weak absorptions near wave numbers characteristic of the *s-trans* rotamer are observed (*e.g.*, see Fig. 3). Since the strain energy in the *s-trans* rotamer is extremely high, it is likely that these absorptions are due to a twisted form. In this connection we should like to mention that, in general, some nonplanar deformations may occur in many structures termed here *s-cis* or *s-trans*; in this sense, the terms "*s-cis*" and "*s-trans*" have only an approximate meaning.

Unlike the β-keto aldehyde enol ethers,[1] β-diketone enol ethers exhibit no extra splitting of the $\nu_{C=O}$ or $\nu_{C=C}$ bands caused by rotation around the C_{sp^2}–O bond, obviously because of additional steric hindrance. The conformation of the =C(R^2)–OR^3 fragment, though not directly accessible, can be estimated from model considerations and the comparison of $\Delta\nu^{C=O}_{C=C}$ values obtained here with those previously[1] found for all possible *s-cis*, *s-trans*, *O-s-cis*, *O-s-trans* conformational combinations in β-keto aldehyde enol ethers.

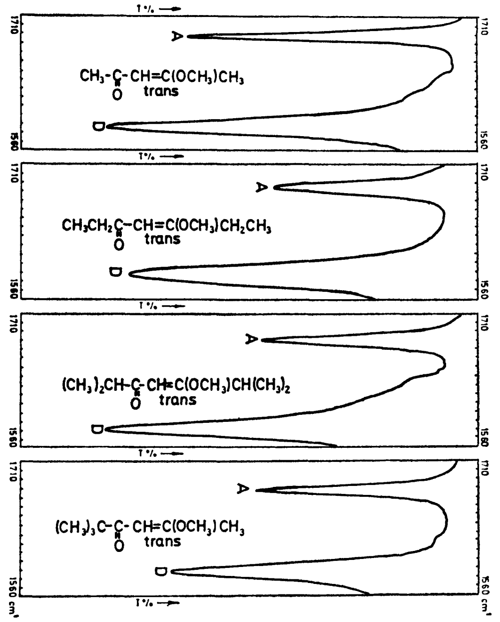


Fig. 3. Infrared spectra of compounds **1** *E*, **2** *E*, **3** *E* and **8** *E* in tetrachloroethylene. Cell thicknesses and concentrations are given in Table 1.

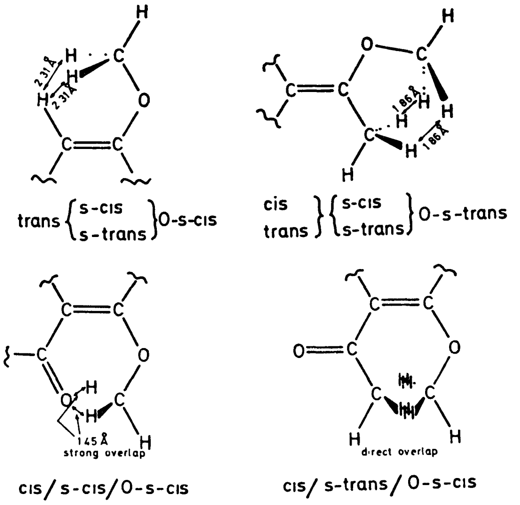


Fig. 4. Interatomic distances in assumed *O-s-cis* and *O-s-trans* conformations of *β*-methoxy compounds. The orientations of methyl groups were chosen to minimize the Pitzer strain energy.

Thus, there is obviously a much weaker non-bonded interaction in the *trans/s-cis/O-s-cis* isomer than in the *trans/s-cis/O-s-trans* one (see formula IV), with the alternative H–H interatomic distance amounting to 2.31 Å *vs.* 1.86 Å (see Fig. 4).† Besides, the *O-s-cis* rotamer is strongly preferred here for electronic reasons.[1,12] Correspondingly, as can be derived from the data of Table 1, the $\Delta\nu^{C=O}_{C=C}$ values lie within the limits of 90—100 cm^{-1}, in excellent agreement with the previous estimation[1] of 80—100 cm^{-1} while the alternative *O-s-trans* conformation requires 75—85 cm^{-1}.

As for the *cis* structures I and II, steric hindrance is important in both *O-s*-conformations, being particularly pronounced in the *O-s-cis* one where a direct overlap of the nearest non-bonded atoms should occur (see Fig. 4). Hence, the anticipated conformation is *O-s-trans*.†† It was of interest to clear up whether the regularities concerning the wave number differences $\Delta\nu^{C=O}_{C=C}$ in the *trans* series[1] hold also for the *cis* isomers. The agreement is again very good as far as the *s-trans* conformation is concerned: the values now found (26—31 cm^{-1}) lie almost exactly within the limits previously established[1] (20—30 cm^{-1}), whereas 35—50 cm^{-1} was found[1] for the alternative *O-s-cis* conformation. On the other hand, the results for the *s-cis* rotamers are less favorable: although the majority of the *O-s-trans* rotamers II exhibit lower $\Delta\nu^{C=O}_{C=C}$ values as compared with the *O-s-cis* rotamers IV (75—94 cm^{-1} *vs.* 90—100 cm^{-1})—a tendency already noticed for keto aldehyde enol ethers, the upper limit of the range now observed (75—94 cm^{-1}) is moved by 9 cm^{-1} above that found[1] for the latter compounds (75—85 cm^{-1}).

PMR Spectra. With the exception of compounds **8** *Z* and *E*, all the enol ethers studied here contain identical groups R^1=R^2, thus the assignment of their signals posed some problems. Anteunis and Schamp[5] examined several unsymmetrically substituted enol ethers (R^1≠R^2) and were able to establish the "ene-one rule", from which it follows that *α* protons of the R^2 group resonate at lower field than *α* protons of the R^1 group. While Anteunis and Schamp[5] were not aware of the *trans* configuration of the compounds studied, it was shown subsequently by Gelin and Rouet[6] that the "ene-one rule" holds for the *trans* structures only, whereas an opposite assignment is true for the *cis* configuration. Assignments coinciding with those by Gelin and Rouet were made by Awang[3] for **1** *E* and *Z* and (apparently intuitively) by Elvidge and Stevens[7] for **2** *E* and *Z*.

Since the term "ene-one rule" refers to the original incomplete assignments by Anteunis and Schamp[5] and might thus be misleading, it seems appropriate to rename the rule as the "ene-one cross-shielding rule". Terminologic problems aside, it should be emphasized that no rationalization was offered for the rule in either of the papers mentioned. The eight *E*, *Z* pairs of compounds, the conformational equilibria of which were established rather reliably, permit us to propose an explanation of the observed phenomena.

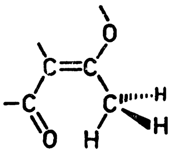
Let us consider first the *trans(E)* isomers of compounds **1**—**7** which, as shown above, all have the *s-cis* conformation (see formula IV on p. 983). Compared with the usual allylic protons, the "ene-side" protons of R^2 are additionally deshielded by both the carbonyl and ether oxygens, whereas the magnetic environment of the "one-side" *α*-protons is practically the same as in the case of typical acylic groups. The resulting

---

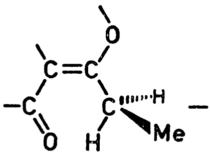
† For details, see our previous paper;[1] the bond lengths and angles have been taken from the paper by Cahill *et al.*[10] and from the tables.[11] As before, the calculations are for R^1=R^2=R^3=Me.

†† It is likely that deviations from planarity may occur not only in the O=C–C=C fragment (*vide supra*) but also in the C=C–OR moiety.

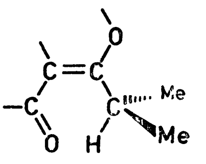
lower-field absorption of R^2 *vs.* R^1 is thus readily explainable. The role of the deshielding of R^2 caused by the carbonyl group is further substantiated by the fact that the δ values increase along with the progressing branching of this substituent:



R^2=Me



R^2=Et

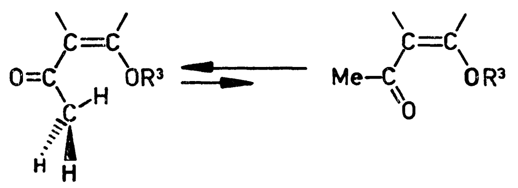


R^2=*i*-Pr

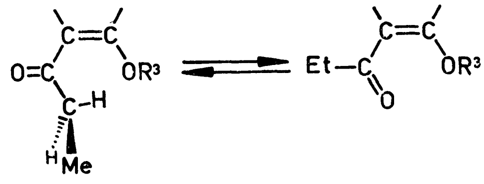
While the deshielding produced by this group, measured as $\Delta\delta^{R^2}_{R^1}$[†††], is assumed to be evenly distributed between the three protons of the rotating methyl group, the average effect should be statistically 3/2 and 3 times greater with R^2=Et and R^3=*i*-Pr, respectively, the rotation of these two groups being severely restricted. The observed increase is in fact even greater, $\Delta\delta^{R^2}_{R^1}$ amounting to 0.15, 0.17 and 0.20 ppm for R^2=Me, 0.35, and 0.34 ppm for R^2=Et, and 1.50 and 1.46 ppm for R^2=*i*-Pr[††††] (see Table 2). This extra increase of $\Delta\delta^{R^2}_{R^1}$ is explainable in terms of a buttressing effect resulting from the interaction between the ether oxygen and the methyls in R^2=Et and R^2=*i*-Pr.

It seems worth noticing that the deshielding of the methine protons of the isopropyl group in **3** *E* and **6** *E* is so strong as to produce a low-field shift even greater than that observed for the α protons of the R^3 group attached to the ether oxygen.

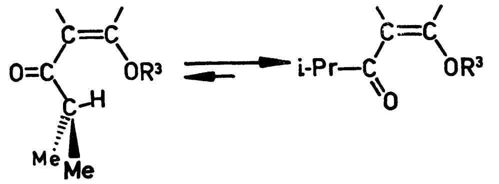
In the *cis(Z)* isomers R^2 is no longer deshielded by the carbonyl oxygen, so it is natural that the acylic protons absorb, as usual, at lower fields than the allylic ones, *i.e.*, $\Delta\delta^{R^2}_{R^1}$ values are negative. These differential shifts are expected to be more negative in the case of the *s-trans* rotamer, due to additional deshielding of R^1 by the alkoxy and olefinic groups. In this connection it might seem surprising that the branching of R_1, which was shown[※] to shift the rotational equilibrium towards the *s-cis* isomer and can thus be anticipated to reduce the additional deshielding just mentioned, leaves the $\Delta\delta^{R^2}_{R^1}$ practically unaffected (see Table 2). It must be taken into account, however, that such branching simultaneously affects the shielding in the opposite direction by a mechanism similar to that discussed above for the *trans* isomer, *i.e.*, by restricting the rotation of the R^1



R^1=Me



R^1=Et



R^1=*i*-Pr

The two effects are apparently compensated in this way.

As for the other NMR signals, only those of the R^3 group seem to be informative. Since the branching of R^1 affects the *s-cis*⇄*s-trans* equilibrium, the constancy of the $\Delta\delta^{E}_{Z}(R^3)$ values within the two series of compounds containing fixed R^3 and varying R^1 suggest that deshielding of R^3 by the carbonyl group in the *cis*/*s-cis* isomer does not play any marked role. Thus, the *cis*/*O-s-trans* or non-planar conformation proposed in the IR part of the present paper receives additional support.

Experimental

cis(Z) *Isomers*: *4-methoxy-3-penten-2-one* (**1** Z), *5-methoxy-4-hepten-3-one* (**2** Z), *and 5-methoxy-2,6-dimethyl-4-hepten-3-one* (**3** Z) were prepared from acetylacetone, dipropionylmethane[13], or diisobutyrylmethane,[14] by treatment with diazomethane as follows: to an excess of an ethereal solution of diazomethane[15] was added 0.05 M of diketone and 10 ml of methanol. The mixture was allowed to stand in dark for 16 h (with **1** *Z* and **2** *Z*) or 24 h (with **3** *Z*). The ether and the unchanged diazomethane were evaporated. Twofold vacuum distillation afforded fairly pure **1** *Z*, bp 37 °C (0.5 Torr), lit,[2] 84—86 °C (10 Torr), lit,[3] 56—58 °C (3.5 Torr), new compounds; data given in Table 3.

cis(Z) *5-Methoxy-2,2-dimethyl-4-hexen-3-one* (**8** Z): The reaction of pivaloylacetone[13] with diazomethane was carried out analogously for 24 h. The fractionate distillation *in vacuo* gave a mixture of isomers (which was not worked up) and an oil which solidified immediately. The resulting solid was pressed on porous porcelain and sublimed two times at 0.3 Torr to yield pure **8** *Z*.

The analogous reaction of diazoethane[15] with acetylacetone, dipropionylmethane, and diisobutyrylmethane in the presence of methanol (reaction time 16 h) gave after sublima-

---

[†††] Since $R^1=R^2$, the use of the differential shifts $\Delta\delta^{R^2}_{R^1}=\delta_{R^2}-\delta_{R^1}$ allows one to eliminate the difficulty arising from the necessity of comparing the methyl, methylene, and methine protons of R^2.

[††††] In order to estimate the deshielding effect of the carbonyl group exerted upon R^2 another differential value concerning the resonance of this group only, *viz.*, $\Delta\delta^{E}_{Z}$, can be used equally successfully. Indeed, the δ_Z values are good reference points for each of the homologues, as they are influenced by all the deshielding factors, the δ_E values are, except for the contribution of the carbonyl group, just now to be found. Numerically, $\Delta\delta^{R^2}_{R^1}$ and $\Delta\delta^{Z}_{E}(R^2)$ are very close.

[※] See the part concerning IR spectra.

Table 3. Physical properties and analytical data

Compound	Bp (°C)	Mp (°C)	%C Calcd	%C Found	%H Calcd	%H Found
2*Z*	51 (0.8 Torr)	—	67.57	67.29	9.93	9.91
2*E*	41 (0.8 Torr)	—				
3*Z*	52 (0.8 Torr)	—	70.54	70.60	10.66	10.78
3*E*	45 (0.8 Torr)	—				
4*Z*	—	41	65.59	65.56	9.44	9.38
4*E*[a)]	76 (15 Torr)	—				
5*Z*	58 (0.8 Torr)	—	69.19	69.20	10.32	10.26
5*E*	42 (0.4 Torr)	—				
6*Z*	53 (0.7 Torr)	—	71.69	71.33	10.94	10.73
6*E*	107 (15 Torr)	—				
7*Z*	53 (0.7 Torr)	—	69.19	69.19	10.32	10.46
7*E*	61 (2 Torr)	—				
8*Z*	—	64	69.19	69.01	10.32	10.30
8*E*	41 (1.3 Torr)	—				

Bp and mp were not corrected. a) This *trans*(*E*) compound was described incorrectly by Giza[4)] to have a *cis*(*Z*) configuration.

tion *4-ethoxy-3-penten-2-one* (**4** *Z*) and, after distillation, *5-ethoxy-4-hepten-3-one* (**5** *Z*) and *5-ethoxy-2,6-dimethyl-4-hepten-3-one* (**6** *Z*), respectively.

A similar treatment of acetylacetone with 1-diazo-2-methylpropane[15)] and methanol yielded *4-isobutoxy-3-penten-2-one* (**7** *Z*).

All the *trans*(*E*) compounds **1**—**8** *E* were prepared by isomerization of their *cis*(*Z*) isomers: the solution of a *cis*(*Z*) isomer in CCl_4 was refluxed for a few hours, then the solvent was removed and the product was distilled *in vacuo*; data given in Table 3.

The physical properties and analytical data of the new compounds and of those whose configuration was not established previously to this paper are given in Table 3.

The structures of all the compounds **1**—**8** *Z* and **1**—**8** *E* were confirmed by NMR spectra (see Table 2). The structures of the unsymmetrical compounds **8** *Z* and *E* were checked additionally by reduction with lithium aluminium hydride:[16)] to a suspension of an excess of $LiAlH_4$ in ether was added **8***E* and the mixture was refluxed for 1.5 h. Water and aqueous potassium hydroxide were added and the mixture was filtered off. The ethereal layer was dried over KOH pellets and worked up in the usual manner to yield *5-methoxy-2,2-dimethyl-4-hexen-3-ol* bp 44—45 °C (0.5 Torr). NMR (δ, ppm in $CDCl_3$): 4.53, d, 1H; 3.50, s, 3H; 1.82, s, 3H; 0.90, s, 9H.

Infrared spectra were recorded on a Perkin-Elmer 325 spectrophotometer with a spectral slit width of 0.7—0.9 cm^{-1} and a scanning speed of 0.25 $cm^{-1}\,s^{-1}$. Commercial "for spectroscopy" solvents were used. The substances investigated were freshly distilled or sublimed before the measurements, and the middle fraction was used. The spectra were calibrated with polystyrene.

NMR spectra were recorded on Varian HA-60/IL and JEOL JNM-4H-100 instruments.

This work is a part of the Polish Academy of Sciences Programme for Structural Research (PAN-3).

References

1) J. Dabrowski and M. Tencer, *Bull. Chem. Soc. Jpn.*, **48**, 1310 (1975).

2) B. Eistert, F. Arndt, L. Loewe, and E. Ayca, *Chem. Ber.*, **84**, 156 (1951).

3) D. V. C. Awang, *Can. J. Chem.*, **49**, 2672 (1971).

4) V. C. Giza, Dissertation, Univ. of Massachusetts, Amherst, Univ. Microfilms, Order No. 64-7123.

5) M. Anteunis and N. Schamp, *Bull. Soc. Chim. Belges*, **76**, 330 (1967).

6) S. Gelin and J. Rouet, *Bull. Soc. Chim. Fr.*, **1971**, 2179.

7) J. A. Elvidge and R. Stevens, *J. Chem. Soc.*, **1965**, 2256.

8) (a) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, **1955**, 3766; (b) E. S. Waight and R. L. Erskine, "Steric Effects in Conjugated Systems," Butterworths, London (1958), p. 73; (c) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, **1960**, 3425; (d) R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960); (e) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 222 (1961); (f) J. Kossanyi, *Bull. Soc. Chim. Fr.*, **1965**, 704; (g) R. Barlet, M. Montagne, and P. Arnaud, *Spectrochim. Acta*, **25A**, 1081 (1969); (h) A. Bienvenue, *J. Am. Chem. Soc.*, **95**, 7345 (1973).

9) (a) J. Dabrowski and K. Kamienska-Trela, *Spectrochim. Acta*, **22**, 211 (1966); (b) J. Dabrowski and U. Dabrowska, *Chem. Ber.*, **101**, 3392 (1968); (c) J. Dabrowski and K. Kamienska-Trela, *Bull. Chem. Soc. Jpn.*, **39**, 2565 (1966); (d) J. Dabrowski and J. Terpinski, *J. Org. Chem.*, **31**, 2159 (1966); (e) J. Dabrowski, K. Kamienska-Trela, and A. J. Sadlej, *J. Mol. Struct.*, **12**, 185 (1972).

10) P. Cahill, L. P. Gold, and N. L. Owen, *J. Chem. Phys.*, **48**, 1620 (1968).

11) Landolt-Bornstein, "Zahlenwerte und Funktionen aus Physik, Chemie…," 2-Teil, Molekeln 1, Springer-Verlag, Berlin (1951), pp. 10—20.

12) B. Cadioli and M. Pinceli, *J. Chem. Soc., Faraday Trans. 2*, **1972**, 991.

13) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).

14) T. Shigematsu, M. Matsui, and K. Utsunomiya, *Bull. Inst. Chem. Res., Kyoto Univ.*, **46**, 256 (1968).

15) B. Eistert, M. Regitz, G. Heck, and H. Schwall, "Methoden der Organischen Chemie," Vol. 10/4, ed. by Houben-Weyl, Georg Thieme-Verlag Stuttgart, West Germany (1968), pp. 537—540.

16) M. Stiles and A. L. Longroy, *J. Org. Chem.*, **32**, 1095 (1967).