# Infrared Spectra and Structure of Substituted Unsaturated Carbonyl Compounds. XIX. Four Component Conformational Equilibria in β-Ketoaldehyde *Trans* Enol Ethers

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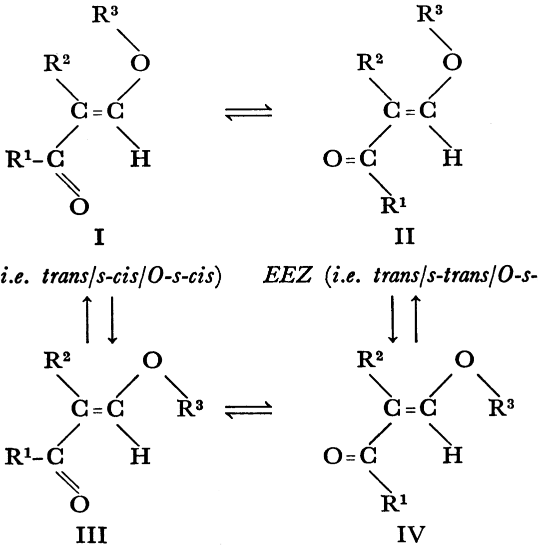
Acylic aliphatic *trans* β-alkoxy-α,β-unsaturated ketones, $R^1COCR^2{=}CHOR^3$, have been shown to exhibit restricted rotation around both the $C_{sp^2}$–$C_{sp^2}$ and $C_{sp^2}$–O single bonds. The conformational equilibria between the *EZZ*, *EEZ*, *EZE* and *EEE* rotamers, estimated from comparison of the IR band intensities, are dependent on the steric requirements of the alkyl substituents. The sequence of the $\nu_{C=O}$ and $\nu_{C=C}$ vibrational frequences is $\nu_{C=O}$(*s-cis*/*O-s-trans*) > $\nu_{C=O}$(*s-cis*/*O-s-cis*) > $\nu_{C=O}$(*s-trans*/*O-s-trans*) > $\nu_{C=O}$(*s-trans*/*O-s-cis*) > $\nu_{C=C}$(*s-trans*/*O-s-trans*) > $\nu_{C=C}$(*s-trans*/*O-s-cis*) > $\nu_{C=C}$(*s-cis*/*O-s-trans*) > $\nu_{C=C}$(*s-cis*/*O-s-cis*). The wave number differences $\Delta\nu^{C=O}_{C=C}=\nu_{C=O}-\nu_{C=C}$ enable to classify the particular compounds according to their conformation in that $\Delta\nu^{C=O}_{C=C}$(*s-cis*/*O-s-trans*) = 75—85 cm$^{-1}$, $\Delta\nu^{C=O}_{C=C}$(*s-cis*/*O-s-cis*) = 80—100 cm$^{-1}$, $\Delta\nu^{C=O}_{C=C}$(*s-trans*/*O-s-trans*) = 20—30 cm$^{-1}$ and $\Delta\nu^{C=O}_{C=C}$(*s-trans*/*O-s-cis*) = 35—50 cm$^{-1}$.

In studies on the rotational isomerism in α,β-unsaturated carbonyl compounds comparatively little attention has been paid to their β-alkoxy derivatives. Eistert *et al.*[1)] were able to isolate the *cis* and *trans* methyl enol ethers of acetyloacetone. Their structure was subsequently confirmed by Awang[2)] in his nuclear Overhauser effect and solvent shift ("ASIS") studies. In the same paper[2)] a choice was made between the possible conformers resulting from restricted rotation around the $C_{sp^2}$–$C_{sp^2}$ single bond, *i.e. s-cis* and *s-trans* rotational isomers. In many cases because of its unfavourable time scale NMR spectroscopy is unsuitable for detecting the individual rotamers and Awang's results must be considered only as an approximation. Therefore, it was of interest to us to study by means of IR spectroscopy a series of β-ketoaldehyde enol ethers capable of existing in these rotational forms. This technique has proved helpful in numerous investigations on rapid rotational equilibria.[3—9)] In the dissertation by Giza[10)] several spectra of β-alkoxy-α,β-unsaturated ketones were published but the resolution was obviously too low to reveal the band splittings observed in our work.

A further reason for the present study was the possibility of the simultaneous occurence of another restricted rotation, *viz.* that around the $C_{sp^2}$–O bond; the latter type of isomerism has been observed[11—13)] in simple vinyl ethers.

## Results and Discussion

As follows from the Introduction, in general, eight stereoisomeric forms are to be expected for β-alkoxy-α,β-unsaturated ketones having formula $R^1COCR^2{=}CHOR^3$. In our study their number is reduced to four however, as in all cases, due to thermodynamic considerations, only the *trans* (*E*) geometrical isomers were obtained. Four isomers are possible because of restricted rotation around the $C_{sp^2}$–$C_{sp^2}$ and $C_{sp^2}$–O single bonds:



I
*EZZ* (*i.e. trans*/*s-cis*/*O-s-cis*)

II
*EEZ* (*i.e. trans*/*s-trans*/*O-s-cis*)

III
*EZE*
(*i.e. trans*/*s-cis*/*O-s-trans*)

IV
*EEE*
(*i.e. trans*/*s-trans*/*O-s-trans*)

Since two IR bands, *viz.*, $\nu_{C=O}$ and $\nu_{C=C}$* are to be expected in the double bond stretching region for each of the isomers, their total number should amount to eight if all the isomers I—IV were present at equilibrium. Such is the case in the spectra of the methyl ketones ($R^1$=Me) **1**, **5**, and **6**. However, in all other cases investigated the number of bands was less, which can be explained either by the absence of some of these isomers or by coincidence of some of their bands.

The experimental data for the solutions in tetrachloroethylene are presented in Table 1.

In order to illustrate the relationship between band intensities and the bulkiness of the substituents $R^1$, $R^2$ and $R^3$ the IR spectra of the appropriate compounds are compared in Figures 1, 2, 4, and 5. The estimation of the populations of the rotamers are based on the reasonable assumption of approximately constant absorbances of the given absorptions for all the compounds investigated.

Let us consider first, for simplicity, the ketones for which the $\nu_{C=O}$ band is split into two components only, *i.e.* those other than **1**, **5**, and **6**. As can be seen from Fig. 1 presenting compounds with constant $R^3$=Me one band in the $\nu_{C=O}$ region (band B) and two bands

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* Although it is obvious that the vibrations of the C=O and C=C groups are strongly coupled, nevertheless the bands, for simplicity, will be called $\nu_{C=O}$ and $\nu_{C=C}$.

TABLE 1. WAVE NUMBERS ($cm^{-1}$) OF ABSORPTION BANDS AND PROBABLE CONFORMATIONAL PREFERENCES OF *trans* $\beta$-ALKOXY-$\alpha,\beta$-UNSATURATED KETONES $R^1COCR^2{=}CHOR^3$ (IN TETRACHLOROETHYLENE)

| Compound | $R_1$ | $R_2$ | $R_3$ | Concentration | Absorption bands[a)] | | | | | | | | Preferred conformation | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\nu_{C=O}$ | | | | $\nu_{C=C}$ | | | | | |
| | | | | | *s-cis* | | *s-trans* | | *s-trans* | | *s-cis* | | $C_{sp^2}$–$C_{sp^2}$ | $C_{sp^2}$–O[b)] |
| | | | | | *O-s-trans* | *O-s-cis* | *O-s-trans* | *O-s-cis* | *O-s-trans* | *O-s-cis* | *O-s-trans* | *O-s-cis* | | |
| | | | | M | $A^1$ | $A^2$ | $B^1$ | $B^2$ | $C^1$ | $C^2$ | $D^1$ | $D^2$ | | |
| **1** | $CH_3$ | H | $CH_3$ | 0.22 | 1697 | 1686 | 1675 | 1662 | 1648 | 1626 | 1615 | 1601 | *s-cis*∼̇*s-trans*[c)] | *O-s-cis*>*O-s-trans*[d)] |
| **2** | $CH_3CH_2$ | H | $CH_3$ | 0.18 | 1697 | | 1673 | | 1645 | 1626 | 1617 | 1603 | *s-cis*∼*s-trans* | *O-s-cis*>*O-s-trans* |
| **3** | $(CH_3)_2CH$ | H | $CH_3$ | 0.17 | 1693 | | 1669 | | 1642 | 1622 | 1611 | 1597 | *s-cis*>*s-trans* | *O-s-cis*>*O-s-trans* |
| **4** | $(CH_3)_3C$ | H | $CH_3$ | 0.14 | 1689 | | ∼1660[e)] | | — | | 1611 | 1596 | *s-cis* | *O-s-cis*>*O-s-trans*[d)] |
| **5** | $CH_3$ | H | $CH_3CH_2$ | 0.18 | 1696 | 1679 | 1672 | 1660 | 1645 | 1622 | 1612 | 1598 | *s-cis*∼*s-trans* | *O-s-cis*∼*O-s-trans* |
| **6** | $CH_3$ | H | $(CH_3)_2CH$ | 0.13 | 1694 | ∼1686 sh | 1668 | ∼1664 sh | 1637 | 1617 | 1609 | 1592 | *s-cis*∼*s-trans* | *O-s-trans*>*O-s-cis* |
| **7** | $(CH_3)_2CH$ | H | $(CH_3)_2CH$ | 0.13 | 1690 | | 1665 | | 1641 | ∼1625 sh | 1610 | 1591 | *s-cis*>*s-trans* | *O-s-trans*>*O-s-cis* |
| **8** | $(CH_3)_3C$ | H | $(CH_3)_2CH$ | 0.12 | 1686 | | ∼1660[e)] | | — | | 1607 | 1591 | *s-cis* | *O-s-trans*>*O-s-cis* |
| **9** | $(CH_3)_3C$ | H | $(CH_3)_3C$ | 0.11 | 1683 | | ∼1660[e)] | | ∼1635[e)] | | 1602 | ∼1588 sh | *s-cis* | *O-s-trans* |
| **10** | $CH_3$ | $CH_3$ | $CH_3$ | 0.17 | 1693 | | 1667 | | 1646 | 1625 | 1615 | 1604 | *s-trans*>*s-cis* | *O-s-trans*∼*O-s-cis* for the *s-cis* isomer<br>*O-s-trans*>*O-s-cis* for the *s-trans* isomer |
| **11** | $CH_3CH_2$ | $CH_3$ | $CH_3$ | 0.17 | 1693 | | 1667 | | 1645 | — | 1617 | — | *s-trans*>*s-cis* | *O-s-trans* |

a) The spectra of all solutions were obtained in a standard cell of thickness 0.1 mm. b) In both the *s-cis* and *s-trans* isomers, if present, except for compound **10**. c) The variable temperature measurements showed some preference of the *s-trans* rotamer. d) Checked by the variable temperature study. e) Weak absorption of a probably non-planar form.

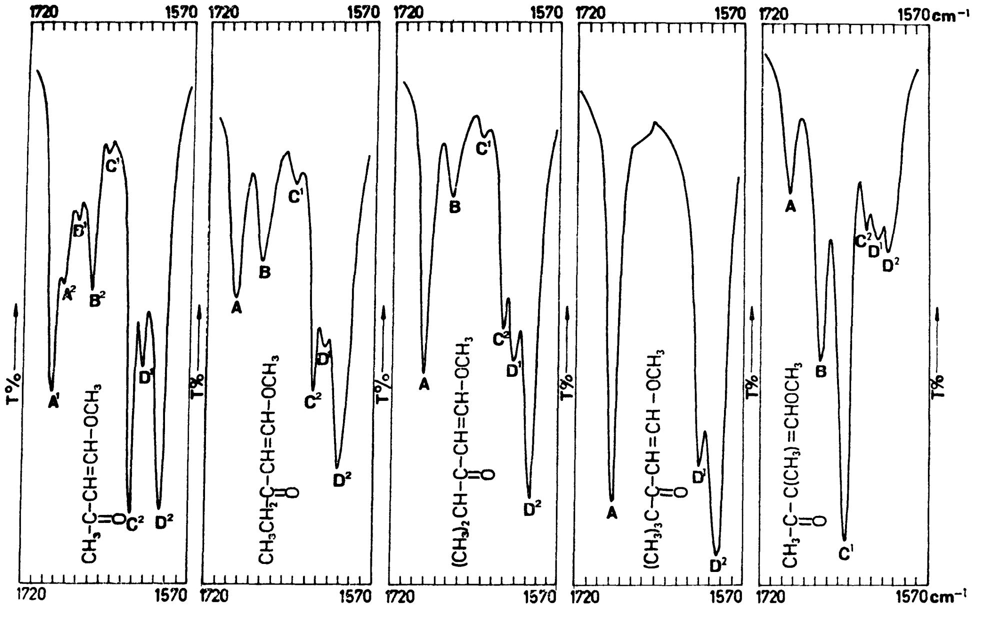

Fig. 1. Infrared spectra of compounds **1**, **2**, **3**, **4**, and **10** in tetrachloroethylene. Cell thicknesses and concentrations are given in Table 1.

in the $\nu_{C=C}$ region (bands $C^1$ and $C^2$) decrease in intensity with increasing size of the substituent $R^1$ in going from compound **2** to **3** and **4** while another $\nu_{C=O}$ band (band A) and two $\nu_{C=C}$ bands ($D^1$ and $D^2$) increase in the same sequence. On the basis of published data concerning other $\alpha,\beta$-unsaturated systems[3–9)] these intensity changes can be attributed to the shift of the equilibrium towards the *s-cis* rotamer due to growing steric interactions between $R^1$ and the $\beta$-hydrogen atom in the *s-trans* rotamer. Therefore, the decreasing bands B, $C^1$ and $C^2$ are assigned here to the $\nu_{C=O}$ and $\nu_{C=C}$ vibrations of the *s-trans* rotamers II and/or IV, and the increasing bands A, $D^1$ and $D^2$ are ascribed to the *s-cis* rotamers I and/or III. As shown further in the text (see the next page) the splittings of the bands C and D result from restricted rotation around the $C_{sp^2}$–O bond. This rotation is also responsible for the splitting of the bands A and B in the spectrum of the methyl ketone **1**.** Taking this splitting into account the band intensities of **1** fit very well to the sequence **1**, **2**, **3** and **4**.

A similar regularity occurs when comparing compounds **6**, **7** and **8**.

Solvent-induced intensity changes are in agreement with these assignments: when passing from hexane to tetrachloroethylene and particularly to the more polar tetrahydrofuran solutions an enhancement of the bands

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** The IR spectrum of **1** has been published,[14)] but no splitting of bands A, B, C and D was reported.

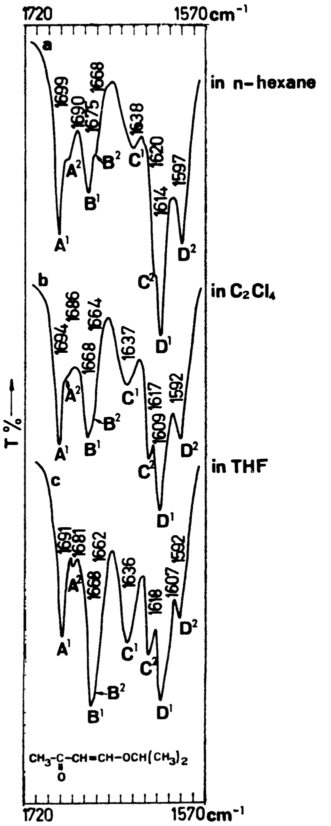


Fig. 2. Infrared spectra of compound **6**. (a) in *n*-hexane (b) in tetrachloroethylene (c) in tetrahydrofuran. Concentrations 0.13 M, cell thicknesses 0.1 mm.

B and C of the more polar *s-trans* form is observed (*e.g.* for **6**; Fig. 2).

The results concerning the *t*-butyl ketones **4**, **8** and **9** are remarkable in that a residual absorption near wave number characteristic of the *s-trans* form is still observed in spite of extremely high strain energy in this form. It seems likely that a twisted form is involved.

If $R^2$ is larger than hydrogen its non-bonded interactions with $R^1$ in the *s-cis* rotamers I and III increase dramatically[15] resulting in an equilibrium shift towards the *s-trans* rotamers II and IV as clearly seen from the relative intensities of the bands B and $C^1+C^2$ *vs.* A and $D^1+D^2$ (*e.g.* for compound **10**, see Fig. 1).

As already mentioned on the foregoing page, we believe that the splitting of bands A, B, C and D into two components is a consequence of the restricted rotation around the $C_{sp^2}$–O bond. This assumption finds convincing support in the intensity changes occuring on varying the steric requirements of the substituent $R^3$ and, in part, of $R^2$ and $R^1$. Like other rotational equilibria, the *O-s-cis*$\rightleftarrows$*O-s-trans* equilibrium is dependent on electronic and steric factors. The latter can be estimated by comparing the corresponding interatomic distances in these two rotamers. Although it is virtually impossible to exactly calculate these distances, the approximation sufficient for the present purposes can be made by adopting the parameters obtained experimentally by Cahill, Gold and Owen[11b] for the *O-s-cis* isomer of the methyl vinyl

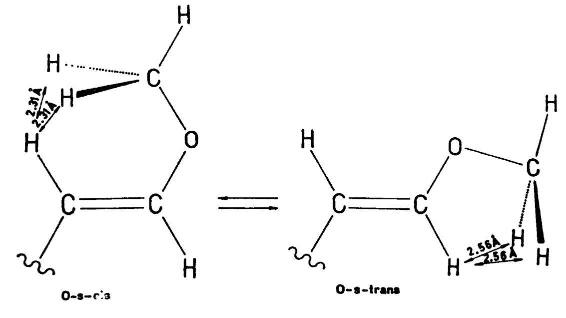


Fig. 3. H–H interatomic distances in *O-s-cis* and *O-s-trans* conformers of methyl enol ethers.

ether. In our analysis equal bond lengths and angles were taken for both the *O-s-cis* and *O-s-trans* conformations and no allowance was made for their distortion (*i.e.* optimalization was not attempted). The interatomic H–H distances were calculated for the most probable orientation of the methyl group. The strain differences thus deduced are undoubtedly even more pronounced for larger $R^3$ groups.

As can be seen from Fig. 3, the interatomic distance between the methyl hydrogens and the nearest vinylic hydrogen is considerably less in the *O-s-cis* rotamer. Nevertheless, this rotamer prevails in the methyl vinyl ether,[11] obviously due to electronic factors.[12]

Let us consider now the splitting of band D in compounds **4**, **8** and **9** having invariable $R^1$=*t*-Bu (see Fig. 4).

In the spectrum of the *O*-methyl derivative **4** the much more intense $\nu_{C=C}$ band $D^2$ can safely be ascribed to the energetically favoured rotamer, as proved by its diminution on raising the temperature. As follows from the above scheme, replacing of R=Me by a bulkier group should shift the equilibrium towards the *O-s-*

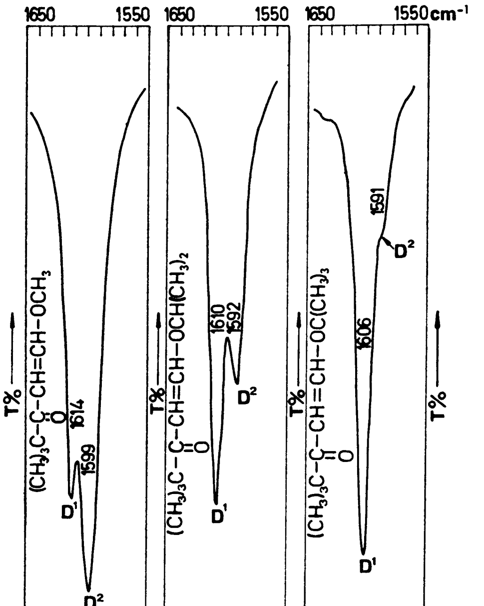


Fig. 4. Infrared spectra of compounds: **4** (concn 0.14 M) **8** (concn 0.12 M) and **9** (concn 0.11 M) in *n*-hexane. Cell thicknesses 0.1 mm.

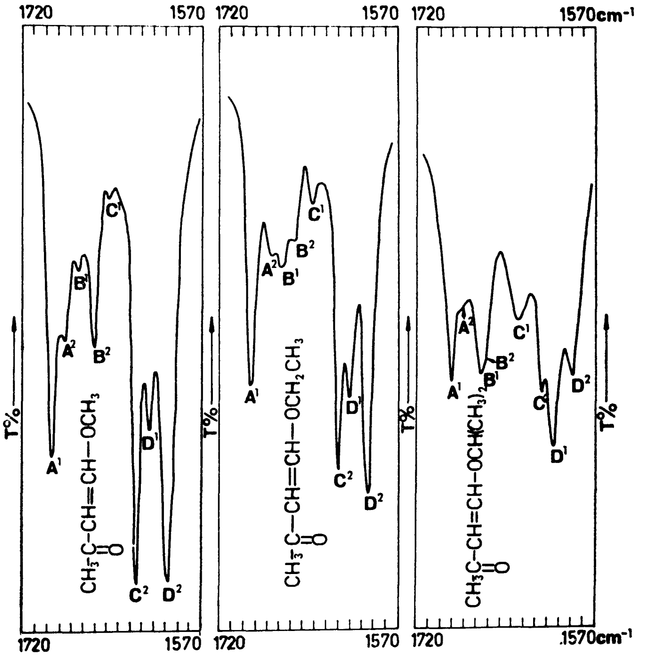


Fig. 5. Infrared spectra of compounds **1**, **5** and **6** in tetrachloroethylene. Concentrations and cell thicknesses are given in Table 1.

*trans* rotamer, assuming the electronic factor to be constant. Accordingly, the $D^1$ band which dramatically increases in the series **4**, **8**, **9** is ascribed here to this rotamer. Band $D^2$ which corresponds thus to the *O-s-cis* rotamer disappears almost completely when $R^3$=*t*-Bu, due to extremely high strain in this form.

Similar splittings and intensity changes due to the restricted rotation around the $C_{sp^2}$–O bond are always observed with band C (if present) and also with bands A and B, provided $R^1$=Me. In the latter case, the high frequency components of all the bands under consideration, *i.e.* $A^1$, $B^1$, $C^1$, and $D^1$, increase on the expense of the $A^2$, $B^2$, $C^2$, and $D^2$ ones along with increasing steric requirements of the $R^3$ group (see Fig. 5). Therefore, the index "1" is assigned to all bands of the *O-s-trans* rotamers and the bands of the *O-s-cis* ones are indexed "2". It should be noted that band $A^1$ of the *O-s-trans* rotamer has a very high absorbance as seen from its higher intensity *vs.* that of band $A^2$ in cases of prevailing *O-s-cis* conformation in **1**. The assignment of bands $A^1$ and $A^2$ is conclusively supported here by the enhancement of the former on the expense of the latter on going to higher temperature.

Substitution of $R^2$=H by a methyl group enhances the steric interactions not only with the substituent $R^1$, which was already discussed above, but also with $R^3$ in the *O-s-cis* isomers I and II. The resulting *O-s-cis→O-s-trans* equilibrium shift manifests itself in the increase of the intensities of bands $C^1$ and $D^1$ on the expense of $C^2$ and $D^2$ if the spectrum of **10** is compared with that of **1**. With the ethyl ketone **11**, the complete disappearance of band $D^2$ is readily explainable by the buttressing effect in the *s-cis* rotamer but no simple explanation can be offered for the simultaneous disappearance of band $C^2$. This point seems to deserve a separate investigation.

The sequence of the $\nu_{C=O}$ and $\nu_{C=C}$ vibrational frequencies proposed here follows that known for other types of unsaturated ketones[3–9] but is further differentiated by taking into consideration the *O-s-cis* and *O-s-trans* rotamers. Thus, $\nu_{C=O}$(*s-cis*/*O-s-trans*) > $\nu_{C=O}$(*s-cis*/*O-s-cis*) > $\nu_{C=O}$(*s-trans*/*O-s-trans*) > $\nu_{C=O}$(*s-trans*/*O-s-cis*) > $\nu_{C=C}$(*s-trans*/*O-s-trans*) > $\nu_{C=C}$(*s-trans-O-s-cis*) > $\nu_{C=C}$(*s-cis*/*O-s-trans*) > $\nu_{C=C}$(*s-cis*/*O-s-cis*). Moreover, the wave number differences $\Delta\nu^{C=O}_{C=C}=\nu_{C=O}-\nu_{C=C}$ corroborate the regularities established by Braude and Timmons[4] and Mecke and Noack[5] enabling at the same time to more precisely classify the particular compounds according to their conformation, especially for the *s-trans* conformation. As can easily be derived from Table 1, $\Delta\nu^{C=O}_{C=C}$(*s-cis*/*O-s-trans*) = 75—85 cm$^{-1}$, $\Delta\nu^{C=O}_{C=C}$(*s-cis*/*O-s-cis*) = 80—100 cm$^{-1}$, $\Delta\nu^{C=O}_{C=C}$(*s–trans*/*O-s-trans*) = 20—30 cm$^{-1}$ and $\Delta\nu^{C=O}_{C=C}$(*s-trans*/*O-s-cis*) = 35—50 cm$^{-1}$.

## Experimental

*4-Methoxy-3-buten-2-one* (**1**), bp 53—54 °C/7 mmHg, lit,[16a] 52—53 °C/4—5 mmHg, *1-methoxy-4-methyl-1-penten-3-one* (**3**), bp 74—75 °C/7 mmHg, lit,[16a] 61—62 °C/3.5 mmHg, *1-methoxy-4,4-dimethyl-1-penten-3-one* (**4**) bp 69—70 °C/5 mmHg, lit,[16a] 61 °C/3 mmHg and *1-methoxy-2-methyl-1-penten-3-one* (**11**), bp 80—81 °C/8 mmHg, lit,[16a] 70°C/4.5 mmHg were obtained according to standard procedure described by Royals and Brannock,[16a] *viz.*, by pyrolysis of the corresponding *β*-ketoaldehyde dimethylacetals[16b,17] in the presence of catalytic amount of sodium methoxide. These reactions, however, were carried out under more vigorous conditions than described in order to obtain products free of starting material. This modification resulted in considerable lowering of the yield.

The same method was applied for obtaining of *1-methoxy-1-penten-3-one* (**2**), bp 65 °C/7 mmHg, lit,[18] 94 °C/15 mmHg from *1,1-dimethoxypentan-3-one*[18] and of *4-methoxy-3-methyl-3-buten-2-one* (**10**), bp 84—85 °C/10 mmHg, lit,[19b] 62—64 °C/4 mmHg, lit,[20] 83—86°C/10 mmHg from *4,4-dimethoxy-3-methylbutan-2-one.*

*4-Ethoxy-3-buten-2-one*(**5**): *1-Diethoxybutan-3-one*[19b] was heated with solid sodium ethoxide (3 per cent by weight) in an oil bath at 190°C while ethanol was removed by distillation at atmospheric pressure. After the distillation of ethanol has been finished (approx. 3 hr), the vacuum distillation was carried out yielding **5**, bp 87—89 °C/17 mmHg, lit,[21] 91—93° C/20 mmHg.

*4-Isopropoxy-3-buten-2-one* (**6**) and *1-isopropoxy-4-methyl-1-penten-3-one* (**7**) were prepared as follows:

To a solution of corresponding chlorovinylketone[22] in 2-propanol cooled to −15 °C an excess of a solution of potassium hydroxide in 2-propanol was dropped. The mixture was then allowed to reach the room temperature, stirred for 4 hr, poured out into water and extracted with ether. The ethereal layer was worked up in usual manner. The distillation *in vacuo* afforded a mixture of **6** or **7** and corresponding diisopropyl *β*-ketoacetal. The mixture thus obtained was heated in a distillation flask with 3 per cent by weight of solid potassium isopropoxide in an oil bath at 190—200 °C, while isopropanol distilled. After loss of 2-propanol had stopped (approx. 4 hr) the product was distilled *in vacuo*, affording **6**, bp 88 °C/15 mmHg lit,[18] 98—102 °C/12 mmHg, lit,[21] 112—118 °C/65 mmHg or **7**.

*1-Isopropoxy-4,4-dimethyl-1-penten-3-one* (**8**): An excess of saturated isopropanolic solution of hydrogen chloride was added to a solution of sodium salt of hydroxymethylenepinacoline (obtained from pinacoline, ethyl formate and sodium) in 2-propanol. The mixture was then stirred for 3 hrs alkalized with 2-propanolic potassium hydroxide, poured out into water and extracted with ether. The ethereal layer was worked up in usual manner. The distillation *in vacuo* afforded a mixture of **8** and corresponding diisopropyl $\beta$-ketoacetal. The mixture was pyrolized in the same manner as described above.

*1-t-Butoxy-4,4-dimethylpenten-1-one-3* (**9**) was obtained by the method analogous to that of Seifert and Schinz[23]: In a flask fitted with a reflux condenser and a water separator was placed hydroxymethylenpinacoline, equimolar amount of *t*-butyl alcohol, catalytic amount of *p*-toluenesulphonic acid and a large excess of benzene. The mixture was boiled for 16 hours while water was removed by azeotropic distillation. The mixture was then washed with aqueous sodium bicarbonate and water and benzene was removed. Vacuum distillation gave an oil which solidified immediately. Twofold sublimation of the resulting solid at 0.8 mmHg gave pure **9**.

Physical properties and analytical data for the three new compounds are given below.

| Compound | Bp (°C/mmHg) | Mp (°C) | %C Calcd (Found) | %H Calcd (Found) |
|---|---|---|---|---|
| **7** | 75—76/3 mmHg | — | 69.19<br>(69.00) | 10.32<br>(10.60) |
| **8** | 71—72/2.5 mmHg | — | 70.54<br>(70.55) | 10.66<br>(10.63) |
| **9** | — | 72 | 71.69<br>(71.74) | 10.94<br>(11.08) |

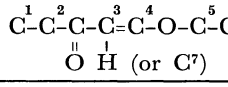
Bp and mp were not corrected.

Structures of all the compounds **1**—**11** were confirmed by NMR spectra (Table 2).

Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer with a spectral slit width of 0.7—0.9 cm$^{-1}$ and a scanning speed of 0.8 cm$^{-1}\cdot$s$^{-1}$. Better spectral parameters gave no better resolution. Commercial "for spectroscopy" solvents were used. The substances investigated were freshly distilled or sublimed before the measurements. Preparative thin layer chromatography was used where necessary. The spectra were calibrated with polystyrene.

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

TABLE 2. $^1$H-NMR CHEMICAL SHIFTS OF $\beta$-KETOALDEHYDE *trans* ENOL ETHERS (ppm; in CCl$_4$)



$$C^{1}-C^{2}-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{H\ (\text{or } C^{7})}}{C^{3}}=C^{4}-O-C^{5}-C^{6}$$

| Compound[a)] | 1 | 2 | 3[b)] | 4[b)] | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| **1** | — | 2.09 | 5.47<br>d | 7.47<br>d | 3.70 | — | — |
| **2** | 1.03<br>t | 2.39<br>q | 5.49<br>d | 7.49<br>d | 3.70 | — | — |
| **3** | 1.08<br>d | 2.57<br>spt | 5.54<br>d | 7.48<br>d | 3.72 | — | — |
| **4** | 1.07 | — | 5.72<br>d | 7.36<br>d | 3.62 | — | — |
| **5** | — | 2.11 | 5.51<br>d | 7.50<br>d | 3.96<br>q | 1.36 | — |
| **6** | — | 2.03 | 5.42<br>d | 7.30<br>d | 4.20<br>spt | 1.23<br>d | — |
| **7** | 1.00<br>d | 2.47<br>spt | 5.49<br>d | 7.31<br>d | 4.17<br>spt | 1.25<br>d | — |
| **8** | 1.13 | — | 5.82<br>d | 7.34<br>d | 4.21<br>spt | 1.32<br>d | — |
| **9** | 1.12 | — | 5.87<br>d | 7.55<br>d | — | 1.40 | — |
| **10** | — | 2.10 | — | 7.10 | 3.83 | — | 1.61 |
| **11** | 1.04<br>t | 2.47<br>q | — | 7.26 | 3.84 | — | 1.63 |

a) See Table 1. b) The coupling constant $J_{34}$ in compounds 1—9 equals 12—13 Hz.

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