sides of Figure 11 indicate how this estimation can be made. Each activation enthalpy $\Delta H^{\ddagger}_{\text{I-1}\rightarrow\text{I-2}}$ and $\Delta H^{\ddagger}_{\text{II-1}'\rightarrow\text{II-2}'}$ can formally be considered as the sum of two enthalpy differences, as indicated in the figure: $\Delta H^{\ddagger}_{\text{I-1}\rightarrow\text{I-2}} = H_{\text{III}} - H_{\text{I}} = (H_{\text{III}} - H_{\text{I}^*}) + (H_{\text{I}^*} - H_{\text{I}})$ and $\Delta H^{\ddagger}_{\text{II-1}'\rightarrow\text{II-2}'} = H_{\text{IV}} - H_{\text{II}} = (H_{\text{IV}} - H_{\text{II}^*}) + (H_{\text{II}^*} - H_{\text{II}})$. The first difference in each of these expressions is the resonance energy of III and IV, respectively, since I* and II* are hypothetical structures with π-bond localization (with normal single and double bonds) and with the same degree of planarity as III and IV. (III and I* are presumed to be planar; IV and II* are presumed to approach planarity as much as is compatible with nonbonding interactions between the inner hydrogens.) The second difference expresses how much energy is required to force the nonplanar ground-state structures I and II into planar or quasiplanar geometries (*i.e.*, into I* and II*, respectively). The energy difference $H_{\text{I}^*} - H_{\text{I}}$ was estimated to be of the order of 3 kcal mol^{-1} or less,[6] the planar Kekulé structure I* thus being higher in energy than the nonplanar ground-state structure I in which the nonbonding interactions between the inner protons and the strain energy are considered to be minimized. The difference $H_{\text{II}^*} - H_{\text{II}}$ could not be estimated since II* (or IV) as well as II have unknown geometries. Most likely II* and IV (and thus II) have very similar geometries and the difference $H_{\text{II}^*} - H_{\text{II}}$ is therefore probably close to zero.

Thus, we can conclude that the resonance energy associated with 20 π electrons delocalized over π-bond systems of geometries such as III (planar, 18 sp^2 carbon atoms) or IV (quasiplanar, 18 sp^2 carbon atoms) is negative and lies between −8.7 and −5 kcal mol^{-1}.

$$\text{RE}\,(20\ \pi\ \text{e}^-/18\ \text{sp}^2\ \text{C}) = -5\ \text{to}\ -8.7\ \text{kcal mol}^{-1}$$

It is interesting to note that resonance energy values of −2.8 kcal mol^{-1} (P. P. P. method) and of −7.2 kcal mol^{-1} (S. P. O. method) were found by semiempirical SCF calculations for the planar [20]annulene (of configuration 439) with delocalized π bonds.[11]

Acknowledgments. We acknowledge, with gratitude, the support of the Schweizerische National Fonds and of the Swiss Chemical Industries (Ciba-Geigy, Lonza, and Hoffmann-La Roche). One of us (E. P. W.) is indebted to the National Research Council of Canada for a Postdoctoral Fellowship (1968–1969). We thank also Dr. J.-M. Gilles for the line-shape calculations.

Conformational Effects of Alkyl Groups on the π → π* Transitions of α-Enones

Alain Bienvenüe

Contribution from Laboratoire de Chimie Organique Physique de l'Université Paris VII, associé au C.N.R.S., 75005 Paris, France. *Received February 21, 1973*

Abstract: The ir and uv spectra (π → π* transition) of 18 cis and trans α-enones, RCOCH=CHMe, have been studied (R = Me, Et, Pr, *i*-Bu, *i*-Pr, *t*-Bu, neoPe, –CH(Me)-*t*-Bu, and –CMe$_2$-*t*-Bu). The molar fractions of all the conformers are calculated from the ir spectra of the enones, assuming that the specific intensities of all the $\nu_{\text{C=O}}$ bands are constants. For trans enones the s-trans ⇌ s-cis equilibrium is displaced toward the s-cis form when R varies in the order Me, Et, Pr, *i*-Bu, neoPe, –CHMe-*t*-Bu, *i*-Pr, *t*-Bu, or –CMe$_2$-*t*-Bu, whereas the cis enones are exclusively s-cis. For R = neoPe, –CH(Me)-*t*-Bu, and –CMe$_2$-*t*-Bu in addition, it has been possible to calculate the contribution of the gauche conformation of R (for enones in the s-cis or in the s-trans forms) where the *t*-Bu substituent does not eclipse the carbonyl. In this conformation one of the Me groups of *t*-Bu is close to the C=C bond and gives rise to $\nu_{\text{C=C}}$ shifts. In the electronic spectrum, a constant $\nu_{\pi\rightarrow\pi^*}$ wave number is found to be associated with each possible set of enone (s-cis or s-trans) and R (eclipsed or gauche) conformations, regardless of the nature of R and the configuration of the enone. When an enone is a mixture of conformations, a linear combination of these $\nu_{\pi\rightarrow\pi^*}$ (using the previously calculated conformer fractions) is shown to give a $\nu_{\max}$ in very good agreement with experimental results. The $\nu_{\max}$ for the s-cis conformation is found to be 2400 cm^{-1} lower than that of the s-trans conformation (47,500 cm^{-1}) and an additional bathochromic shift of 800 cm^{-1} is observed when a Me group is close to the C=C bond.

Woodward's rules,[1] which relate the position of the π → π* transition to the number of alkyl substituents in the R_α, $\text{R}_{\beta c}$, or $\text{R}_{\beta t}$ positions of enones, are well known, and their analytical utility is beyond question. It is curious, however, to note that there have been few attempts to explain them theoretically. The following are two typical approaches: that of Allinger, *et al.*,[2] who apply a modified Pariser–Parr treatment to cyclic enones in conformations approximating to s-cis or s-trans; that of Luft and Basso[3] who calculate by a *w*, *w′*, *w′′* SCF method the effect of progressively substituting hydrogen atoms by methyl groups in the skeleton MeCOC=C. The two calculations lead to results no closer to experimental values (about 2–5 nm) than Woodward's empirical rules. It is likely that these differences are caused in part by the failure to take into account the variations of the bond angles in cyclic systems or the conformational modifications imposed by substitution in labile system.

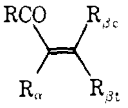
---

(1) R. B. Woodward, *J. Amer. Chem. Soc.*, 63, 1123 (1941).

(2) N. L. Allinger, T. W. Stuart, and J. C. Tai, *ibid.*, 90, 2809 (1968).

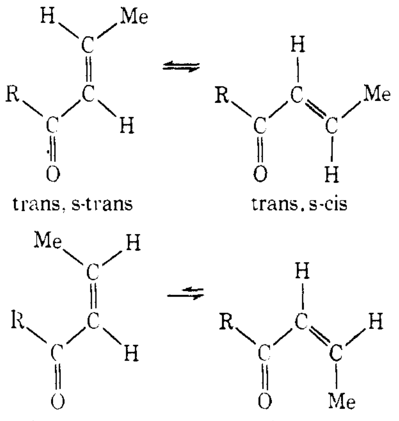
(3) R. Luft and J. Basso, *C. R. Acad. Sci., Ser. C*, 265, 980 (1967).

We have shown,[4] in an earlier study of the $\pi \rightarrow \pi^*$ transition of trans enones RCOCH=CHR$_{\beta t}$ in hexane, that the nature of the R group markedly influences the electronic spectrum of these compounds. There is, for



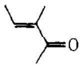
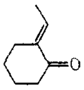
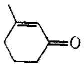
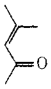
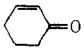
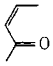
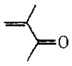
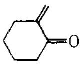
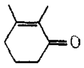
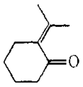
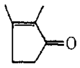
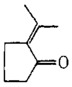
example, a 2400 cm^{-1} shift in $\nu_{\pi-\pi^*}$ in going from R = Me to R = Tm (or tetramethylpropyl), and this shift is independent of the nature of R$_{\beta t}$ (which varies from H to neoPe and *t*-Bu). Neither Woodward's rules nor semitheoretical calculations predict an effect of this magnitude. We have therefore chosen to investigate enones in which ring strain is absent, which means that they are probably in conformational equilibrium. This equilibrium can be observed by ir spectroscopy, since temperature studies on the vibrational spectra of enones clearly show that the spectral modifications are due to conformational changes.[5]

The purpose of the present work was to examine the nature of the effects of R on $\nu_{\pi\rightarrow\pi^*}$, knowing in advance that inductive or steric constants[6,7] give little useful information.[4] The question is the following. Is the effect of R electronic or can the influence of R on the conformational equilibrium s-trans $\rightleftharpoons$ s-cis explain the $\nu_{\pi\rightarrow\pi^*}$ shifts? Existing data on the locked conformations (Table I) show that $\nu_{\pi\rightarrow\pi^*}{}^{\text{s-trans}}$ is higher than $\nu_{\pi\rightarrow\pi^*}{}^{\text{s-cis}}$ but the difference between these two frequencies is not constant probably because other factors, such as ring strain, also have a bearing on the frequency.



We investigated the ir and uv spectra of two series of 9 α-enones RCOCH=CHMe trans (**1t**, R = Me; **2t**, R = Et; **3t**, R = Pr; **4t**, R = *i*-Bu; **5t**, R = *i*-Pr; **6t**, R = *t*-Bu; **7t**, R = neoPe; **8t**, R = -CH(Me)-*t*-Bu; **9t**, R = Tm) and cis (**1c**–**9c** with R in the same order as for the trans series). In the cis series, all the enones are probably s-cis as is the case for 3-penten-2-one[8,9] where R = Me. However, in the trans series, on the other hand, it has been shown that the conformational equilibrium s-trans $\rightleftharpoons$ s-cis favors the s-cis form as R increases in size.[10] We shall now endeavor to interpret the $\pi \rightarrow \pi^*$ shifts (measured in hexane, a solvent where solute–solvent interactions are very weak) in light of the structural information provided by the ir data.

Table I. Comparison of $\nu_{\pi\rightarrow\pi^*}$ Wave Numbers for Locked Conformations

s-Trans compd	ν, cm^{-1}	s-Cis compd	ν, cm^{-1}	Solvent	$\Delta\nu$, cm^{-1}
	44,840[a]		42,020[b]	Hexane	2820
	44,440[b]		43,280[c]	Hexane	1160
	45,870[b]		45,130[d]	Hexane	740
	45,850[c]		43,480[e]	Ethanol	2370
	42,730[b]		40,900[f]	Hexane	2830
	42,730[g]		36,500[h]	Ethanol	3230

[a] F. H. Cottee, B. P. Straughan, C. J. Timmons, W. F. Forbes, and R. Shilton, *J. Chem. Soc. B*, 1146 (1967). [b] See ref 8. [c] A. Bienvenüe, Thèse doctorat ès sciences, Paris, 1969. [d] See Table III. [e] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960). [f] E. S. Waight and R. L. Erskine in "Steric Effects in Conjugated Systems," Butterworths, London, 1958. [g] H. N. A. Al-Jallo and E. S. Waight, *J. Chem. Soc. B*, 73 (1966). [h] W. M. Schubert and W. A. Sweeney, *J. Amer. Chem. Soc.*, **77**, 2297 (1955).

Results

Ir and uv spectroscopic data are given in Tables II and III (see Experimental Section for details).

Discussion

Conformational Analysis of Enones 1–6 (cis and trans). The position and the intensity of the ir bands $\nu_{C=O}$ and $\nu_{C=C}$ are used to identify the conformations as follows.[8,11] Firstly, the bands appear in the order of decreasing wave number, $\nu_{C=O}{}^{\text{s-cis}}$, $\nu_{C=O}{}^{\text{s-trans}}$, $\nu_{C=C}{}^{\text{s-trans}}$, and $\nu_{C=C}{}^{\text{s-cis}}$, and secondly the ratio of the intensities $I_{C=O}$ and $I_{C=C}$ is of the order of 10 for s-trans conformations and of the order of 1 for s-cis conformations.[12] Clearly, this approach is only valid when it is possible to distinguish the four C=O and C=C absorptions. However, in some enones, which we shall discuss later, when R contains an α-*tert*-butyl group, the spectra are more complicated. We shall therefore

---

(4) A. Bienvenüe and J. E. Dubois, *J. Chim. Phys.*, 623 (1972).

(5) (a) R. N. Jones and K. Noack, *Can. J. Chem.*, **39**, 2214 (1961); (b) A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc. B*, 810 (1969).

(6) R. W. Taft, Jr, in "Steric Effects in Organic Chemistry," M. S. Newmann, Ed., Wiley, New York, N. Y., 1956.

(7) C. K. Hancock, E. A. Meyers, and B. J. Yager, *J. Amer. Chem. Soc.*, **83**, 4211 (1961).

(8) R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

(9) J. E. Baldwin, *J. Org. Chem.*, **30**, 2423 (1965).

(10) (a) J. Kossanyi, *Bull. Soc. Chim. Fr.*, 704 (1965); (b) G. Sturtz, *ibid.*, 2477 (1967); (c) W. P. Hayes and C. J. Timmons, *Spectrochim. Acta, Part A*, **24**, 323 (1968).

(11) R. Barlet, M. Montagné, and P. Arnaud, *Spectrochim. Acta, Part A*, **25**, 1081 (1969).

(12) *I* is the measured or apparent intensity of a band, defined by $I = 1/cl\int A(\nu)\, d\nu$, where *c* is the measured concentration of the solute (in mol l.$^{-1}$) and *l* the thickness of the cell (in cm); $A(\nu)$ is the absorbance of the sample at the wave number ν. In the case where the solute exists in two conformations *i* is the specific intensity defined by $i = I/x$, where *x* is the molar ratio of this conformer.

Table II. The Electronic Spectra of Cis and Trans Enones in Hexane

Trans enones						Cis enones					
Enone no.	ν^a	ϵ^b	$W_{1/2}{}^a$	Dis^{a,c}	$\nu_{\text{calcd}}{}^d$	Enone no.	ν^a	ϵ^b	$W_{1/2}{}^a$	Dis^{a,c}	$\nu_{\text{calcd}}{}^d$
1t	46,700	11,800	5600	790		**1c**	45,130	8,500			
2t	46,490	12,200	6020	840		**2c**^{e}	45,290	10,200	5530	750	
3t	46,320	12,400	5870	790		**3c**	45,130	9,450	5900	900	
4t	46,110	13,800	6270	1030		**4c**	45,050	9,850	5710	910	
5t	45,890	10,900	5790	510		**5c**	45,090	9,600	5440	760	
6t	45,080	11,100	5510	710		**6c**	45,040	8,600	5600	860	
7t	45,620	10,800	6040	840	45,470	**7c**	44,660	9,700	5640	820	44,570
8t	45,390	11,300	6360	900	45,270	**8c**	44,380	10,000	5530	910	44,300
9t	44,290	11,500	5730	930		**9c**	44,310	10,300	5410	890	
Mean value			5870	820					5600	850	
Estd error			±400	±250					±300	±100	

[a] In cm^{-1}. [b] In l. mol^{-1} cm^{-1}. [c] Half height dissymmetry of the $\pi \rightarrow \pi^*$ band. [d] Frequency calculated from eq 10 (*vide infra*). [e] This compound contains about 2–3% of an unknown product which could not be separated by vpc.

Table III. The Ir Spectra of Cis and Trans Enones in Hexane

Enone no.	ν^a	I^b	Enone no.	ν^a	I^b	Enone no.	ν^a	I^b	Enone no.	ν^a	I^b
1t	1705	1600	**1c**	1699^c	3610^c	**6t**	1697	5400	**6c**	1692	5000
	1684	5770		1707^d			1632	6400		1620	3100
	1645	220		1618^c	2300^c						
	1634	2100		1621^d							
2t	1707	2480	**2c**	1702	4250	**7t**	1708	530	**7c**	1702	2340
	1685	5100		1625	3000		1697	2500		1691	3000
	1646	200					1688	1060		1633	380
	1636	3100					1672	2700		1616	3800
							1646	300			
							1637	330			
							1630	3470			
3t	1706	2740	**3c**	1698	4750	**8t**	1715	320	**8c**	1692	3660
	1684	2920		1621	3020		1699	2500		1683	470
	1679	1450					1693	320		1618	2570
	1647	240					1676	1000		1612	530
	1637	2840					1672	2000			
	1629	530					1645	290			
							1631	3740			
							1623	760			
4t	1703	3340	**4c**	1698	4200	**9t**	1688	4000	**9c**	1682	4900
	1683	3760		1622	2560		1626	6300		1614	3260
	1674	590									
	1648	100									
	1636	3920									
5t	1703	3920	**5c**	1698	4750						
	1682	2770		1622	3120						
	1636	3560									

[a] In cm^{-1}. [b] Specific intensity in 10^5 cm mol^{-1}. [c] See ref 6. [d] See ref 11.

consider first of all compounds **1t**–**6t** and **1c**–**6c** in which this feature is absent. The different bands of these trans enones have been assigned to the s-trans and s-cis conformations (Table IV). The two band spectra of the cis enones allow us to infer that all these enones have the cis conformation.[13,14]

For trans enones, where there are four absorptions, it is necessary to calculate the relative importance of each conformation. It is known from ir results on locked conformations that the specific intensities $i_{\text{C=O}}{}^{\text{s-trans}}$ are greater than $i_{\text{C=O}}{}^{\text{s-cis}}$,[8,11] but until now no attempts have been made to estimate the values of these intensities.

For this reason the molar fractions $x^{\text{s-cis}}$ and $x^{\text{s-trans}}$ have not previously been calculated from ir data. It seems, however, reasonable to assume that, in a given series of compounds, the intensities $i_{\text{C=O}}{}^{\text{s-trans}}$ and $i_{\text{C=O}}{}^{\text{s-cis}}$ are constant. Now, eq 1, 2, and 3 lead to eq 4 which must be satisfied if the hypothesis is valid. Consistent with this hypothesis, a very good fit (r = 0.997) is obtained for the enones **1t**–**6t** with $i_{\text{C=O}}{}^{\text{s-trans}}$ = 8800, $i_{\text{C=O}}{}^{\text{s-trans}}/i_{\text{C=O}}{}^{\text{s-cis}}$ = 1.6, and thus $i_{\text{C=O}}{}^{\text{s-cis}}$ = 5500.[15] We are now able to calculate from eq 2 and 3 the molar ratios which appear in Table IV. We have adjusted their values so that eq 1 is obeyed exactly.

$$x^{\text{s-trans}} + x^{\text{s-cis}} = 1 \tag{1}$$

$$x^{\text{s-trans}} = I_{\text{C=O}}{}^{\text{s-trans}}/i_{\text{C=O}}{}^{\text{s-trans}} \tag{2}$$

$$x^{\text{s-cis}} = I_{\text{C=O}}{}^{\text{s-cis}}/i_{\text{C=O}}{}^{\text{s-cis}} \tag{3}$$

$$I_{\text{C=O}}{}^{\text{s-trans}} = -(i_{\text{C=O}}{}^{\text{s-trans}}/i_{\text{C=O}}{}^{\text{s-cis}})I_{\text{C=O}}{}^{\text{s-cis}} + i_{\text{C=O}}{}^{\text{s-trans}} \tag{4}$$

---

(13) The s-trans conformations are probably planar; the s-cis conformations, on the other hand, are unlikely to be exactly planar. However, the quasiconstancy of the transmission of electronic effects in s-trans and s-cis conformers of some ring substituted *trans*-cinnamoyl ketones[14] and the small variation of $\epsilon_{\pi\rightarrow\pi^*}$ for enones suggest that they are not far from planarity.

(14) W. F. Winecoff and D. W. Boykin, *J. Org. Chem.*, 37, 674 (1972).

(15) Application of this method to other analogous results[10c] gives also an excellent fit.

Table IV. Conformational Assignment of Ir Bands (Enones **1–6c** and **t**)

Trans enones				Cis enones			
Enone no.	ν^a	$x^{\text{s-cis}}$	K	Enone no.	ν^a	Assignment	$\Delta\nu^{a,b}$
1t	1705	0.31	0.45	**1c**	1699[c]	C=O s-cis	6
	1684					C=O s-trans	
	1645					C=C s-trans	
	1634				1618[c]	C=C s-cis	16
2t	1707	0.44	0.79	**2c**	1702	C=O s-cis	5
	1685					C=O s-trans	
	1646					C=C s-trans	
	1636				1625	C=C s-cis	11
3t	1706	0.50	1	**3c**	1698	C=O s-cis	7
	1684					C=O s-trans	
	1679[d]					C=O s-trans	
	1647					C=C s-trans	
	1637				1621	C=C s-cis	16
	1629					C=C s-cis	
4t	1703	0.55	1.22	**4c**	1698	C=O s-cis	5
	1683					C=O s-trans	
	1674[d]					C=O s-trans	
	1648					C=C s-trans	
	1636				1622	C=C s-cis	14
5t	1703	0.70	2.3	**5c**	1698	C=O s-cis	5
	1682					C=O s-trans	
	1636				1622	C=C s-cis	14
6t	1697	1	>100	**6c**	1692	C=O s-cis	5
	1632				1620	C=C s-cis	

[a] In cm^{-1}. [b] $\nu_{\text{trans}} - \nu_{\text{cis}}$ for a given conformation. [c] See ref 6. [d] Bands of weak intensity, which probably have the same origin as the lowest wave number bands observed when R = neoPe or CH(Me)-*t*-Bu, and assigned to the gauche conformation of R (see Table V).

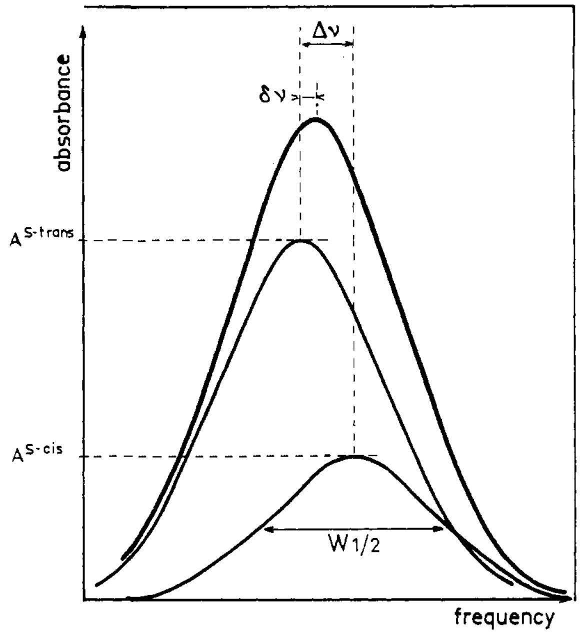


Figure 1. A mathematical model for the sum of the absorption curves of s-trans and s-cis conformers.

The increase in the importance of the s-cis conformer with the steric requirement of R, which has already been observed,[10] is seen to be confirmed quantitatively but also more systematically than in previous studies. While it is almost certain that the origin of this effect is steric, correlations between the logarithm of the equilibrium constant $K = x^{\text{s-cis}}/x^{\text{s-trans}}$ and the steric parameters E_S[6] or $E_S{}^C$[7] are unsatisfactory. Now that the molar fractions of s-cis and s-trans conformers have been determined by ir spectroscopy, we propose to study the effect of this conformational equilibrium on the $\pi \rightarrow \pi^*$ absorption in the electronic spectrum.

Influence of Conformation on Electronic Spectra. In this section, the $\nu_{\pi\rightarrow\pi^*}$ wave numbers of the enones **1–6** (cis and trans) are studied. All the purely s-cis enones (**6t** and **1–6c**) have the same value, $\nu_{\pi\rightarrow\pi^*}{}^{\text{s-cis}} =$ 45,100 cm^{-1}. If we make the reasonable assumption that the s-trans conformation of all enones would also have a constant wave number $\nu_{\pi\rightarrow\pi^*}{}^{\text{s-trans}}$, the effect of R on $\nu_{\pi\rightarrow\pi^*}$ would be due only to the influence of this group on the conformational equilibrium. Any enone, such as the trans enones **1–5t**, which has two conformers gives then a $\pi \rightarrow \pi^*$ band which is the sum of the bands associated with the s-cis and s-trans conformations.

It can be noted at the outset that $\epsilon_{\pi\rightarrow\pi^*}$ and $W_{1/2}$ do not vary appreciably (see Table II)[16] and, moreover, that double maxima or even shoulders in the broad band are never observed. It must be that $\Delta\nu_{\pi\rightarrow\pi^*} = \nu^{\text{s-trans}} - \nu^{\text{s-cis}}$ is less than half of $W_{1/2}$ (the calculations confirm this assertion) and that $\epsilon_{\pi\rightarrow\pi^*}$ and $W_{1/2}$ of the s-cis and s-trans absorption curves are approximately equal. The separation between the maxima of these two curves is unknown, but it is possible to calculate the sum of two Gaussian[19] curves so that both curves having the same $W_{1/2}$ and $\Delta\nu_{\pi\rightarrow\pi^*}$ distances are different and the sum of their maximum absorbance $A^{\text{s-cis}}$ and $A^{\text{s-trans}}$ is a constant (Figure 1).

---

(16) $\epsilon_{\pi\rightarrow\pi^*}$ is in fact approximately constant only for trans enones. Cis enones have generally slightly lower ϵ, perhaps because the proximity of the cis Me to the carbonyl oxygen causes some distortion from the planar structure. This proposal is in agreement with the value of about 30° for the angle between the C=O and the C=C planes in mesityl oxide[17] where there is also a cis Me. The uv results of Table II seem to show that this possible distortion does not affect appreciably the $\nu_{\pi\rightarrow\pi^*}$ values. In a similar way, the cis and trans enones *t*-BuCOCH=CH-*t*-Bu have the same $\nu_{\pi\rightarrow\pi^*}$,[18] while the former is s-cis and the latter probably gauche s-cis.

(17) D. Iszak and R. J. W. Lefevre, *J. Chem. Soc.*, **3**, 251 (1966).

(18) K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kobodny, K. K. Kronberger, and D. K. Roc, *J. Amer. Chem. Soc.*, **92**, 2783 (1970).

(19) A Gaussian shape fits best the experimental curve of the entirely s-cis enones.

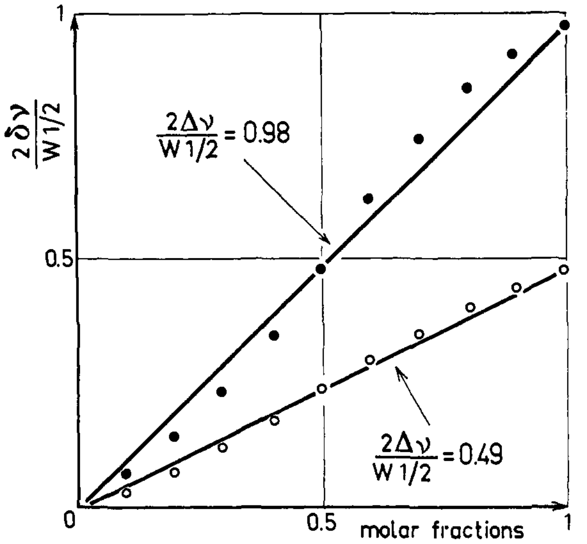


Figure 2. Quasilinear relationships between $\delta\nu_{max}$ (displacement of ν_{max} of the curve obtained by addition of s-cis and s-trans absorption curves) and the molar fractions of conformers.

The calculation shows that the half-height width, the maximum absorbance, and the dissymmetry of the overall curve do not vary very much (maximum variations are 10, 8, and 4%, respectively, when $\Delta\nu_{\pi\rightarrow\pi^*}$ approaches half $W_{1/2}$). Moreover, the maximum frequency is a nearly linear function of the molar ratio $x^{s\text{-}cis}$. The deviations from the straight line increase with the ratio $2\Delta\nu_{\pi\rightarrow\pi^*}/W_{1/2}$ but are never greater than 6% of $\Delta\nu_{\pi\rightarrow\pi^*}$ (see Figure 2).

The results of the calculations show that $\nu_{\pi\rightarrow\pi^*}{}^{exp}$ must be a linear function of the molar fraction $x^{s\text{-}cis}$, as is demonstrated in Figure 3. This result therefore supports the hypothesis that $\Delta\nu_{\pi\rightarrow\pi^*}$ is constant. The extrapolation of the straight line in Figure 3 gives the value of $\nu_{\pi\rightarrow\pi^*}{}^{s\text{-}trans} = 47{,}500$ cm^{-1} and also the value of $\Delta\nu_{\pi\rightarrow\pi^*} = 2400$ cm^{-1}, which were not directly accessible. Semiempirical calculations on butadiene give values of the same order of magnitude (2400[20] and 3700 cm^{-1} [21]); this system is analogous to the enones with the important difference that there are no alkyl group effects to take into account.

These results can be taken as evidence that the shift of $\nu_{\pi\rightarrow\pi^*}$ when the size of R increases is caused by a displacement of the conformational equilibrium between the s-cis and s-trans forms.

Conformations of Groups (R = neoPe, -CH(Me)-*t*-Bu, and -CMe$_2$-*t*-Bu). In the ir spectra of enones **7-9** (c and t) where R = neoPe and -CH(Me)-*t*-Bu, there are generally more than two C=O or C=C bands associated with the s-cis and s-trans conformations (see Table III). The same kind of result is obtained with the C=O bands of saturated ketones, aldehydes, or *N*,*N*-dimethylamides for the same substituents. Furthermore, the relative intensities of these bands are temperature and solvent dependent, thus excluding the possibility that this phenomenon is due to Fermi resonance.[22] For R = neoPe and -CH(Me)-*t*-Bu, two C=O bands about 10-15 cm^{-1} apart are observed. Their identification is based on the following results: firstly, in the case of aldehydes R$_1$R$_2$CHCHO, an nmr study[23] has shown that there is an equilibrium between three conformers, differing in the nature of the substituent in the plane of the carbonyl; secondly, it has been shown[24] that $\nu_{C=O}$ of diethyl ketone is shifted to lower wave numbers when a Me is rotated out of the plane of the carbonyl group. By generalization of these results to carbonyl compounds other than aldehydes and to R alkyl groups other than Me, we may assign the higher wave number $\nu_{C=O}$ band to an E conformation of R, where *t*-Bu eclipses the carbonyl group; the other band corresponds to a G conformation where the *t*-Bu is gauche with respect to the carbonyl plane (see Figure 4). When R = -CMe$_2$-*t*-Bu there is only one absorption and on the basis of the observed wave numbers of the E and G conformations[25] it is possible to conclude that this group is entirely in the G conformation.

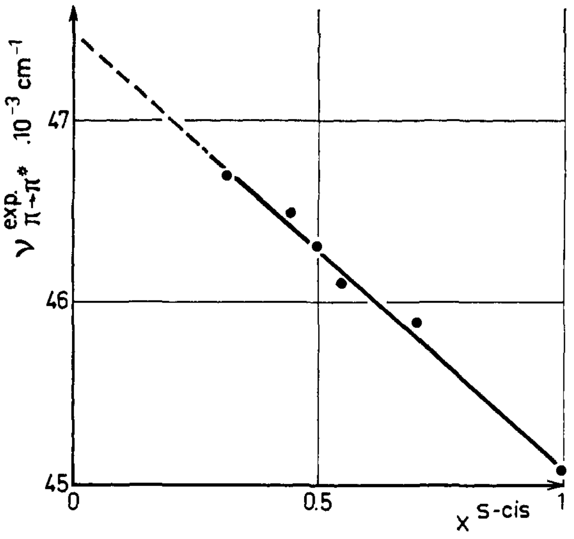


Figure 3. Linear relationships between $\nu_{\pi\rightarrow\pi^*}{}^{exp}$ for trans enones **1-6t** and the molar fraction of the s-cis conformer as measured by ir spectroscopy. The straight line ($r = 0.996$) has the eq $\nu_{\pi\rightarrow\pi^*}{}^{exp} = -2360\,\nu^{s-cis} + 47500$.

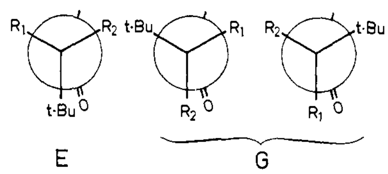


Figure 4. Conformations of R with a *t*-Bu α to the carbonyl. In the case where R^1 = Me and R^2 = H, the G conformer may exist in two conformations.

In the same way it has been possible to establish the conformational assignment of every $\nu_{C=O}$ band observed (Table V) in the spectra of the α-enones **7-9** (c and t), the s-cis and s-trans conformations also being taken into account. The $\nu_{C=C}$ bands for these enones are more complex than those of enones **1-6** (c and t)

---

(20) J. N. Murrell in "The Theory of the Electronic Spectra of Organic Molecules," Chapman and Hall, London, 1971, p 150.

(21) N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **86**, 2811 (1964).

(22) J. E. Dubois, A. Massat, and P. Guillaume, to be submitted for publication.

(23) G. J. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, **87**, 2864 (1965).

(24) R. E. Davis, C. R. Chuang-Pfaffenberger, D. J. Gros, and J. V. Morris, *Tetrahedron*, **25**, 1175 (1969).

(25) J. E. Dubois, A. Massat, and P. Guillaume, *J. Mol. Struct.*, 4, 403 (1969).

Table V. Enones with R = neoPe, –CH(Me)-*t*-Bu, and Tm, Conformational Assignment of Ir Bands and Molar Ratios of the Conformers[a]

Trans enones				Cis enones					
No.	ν	x_R[b]	x[c]	No.	ν	x_R[b]	x[c]	Assignment	$\Delta\nu$[d]
7t	1708	0.07		**7c**	1702	0.34	1	C=O s-cis E	6
	1697	0.50	0.57		1691	0.66		C=O s-cis G	6
	1688	0.09						C=O s-trans E	
	1672	0.34						C=O s-trans G	
	1646							C=C s-trans G	
	1637				1630			C=C s-cis E	7
	1630				1616			C=C s-cis G	14
8t	1715	0.05		**8c**				C=O s-cis E	
	1699	0.59	0.64		1692	1	1	C=O s-cis G	7
	1693				1683				10
	1676	0.09						C=O s-trans E	
	1672	0.27						C=O s-trans G	
	1645							C=C s-trans	
	1631				1618			C=C s-cis E	5
	1623				1612			C=C s-cis G	11
9t	1688	1	1	**9c**	1682	1	1	C=O s-cis G	6
	1626				1614			C=C s-cis G	12

[a] Wave numbers in cm^{-1}. [b] Molar fraction of each conformer of R for a given s-cis of s-trans conformation. [c] Molar fraction of s-cis conformer (R either in E or G conformation). [d] Difference between ν_{trans} and ν_{cis} for a given conformation. The conformational assignments are confirmed by comparison with the corresponding values in Table IV.

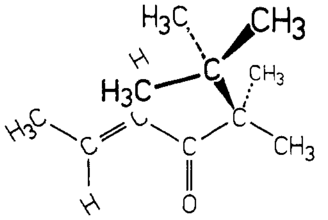


Figure 5. Proximity of one Me group, β to the carbonyl, and the C=C bond when R has the G conformation (R = Tm).

(see Tables III–V). Enones **9** (t and c), where R is in the G conformation, give a $\nu_{C=C}{}^{\text{s-cis}}$ band 6 cm^{-1} lower than enones **6** (t or c) where R is also a tertiary group. The same difference exists between the main $\nu_{C=C}{}^{\text{s-cis}}$ band of **7–8** (t or c), where R is predominantly in the G conformation, and the $\nu_{C=C}{}^{\text{s-cis}}$ of **1–5** (t or c).

There is probably a correlation between the existence of the G conformation and the shift of $\nu_{C=C}{}^{\text{s-cis}}$, which can, tentatively, be attributed to the proximity of one of the terminal Me groups of *t*-Bu to the C=C bond (see Figure 5). An analogous shift of $\nu_{C=C}{}^{\text{s-cis}}$ was observed for the enones MeCOCH = C(neoPe)$_2$ [11] for which Arnaud, *et al.*[26] suppose the conformation is such that the terminal methyls of the neoPe groups are near the C=C bond.

In order to calculate the molar ratio of s-cis and s-trans conformers, and for each of them the molar fraction of E and G conformers, we write eq 5 and 6. We suppose that the ratio of the specific intensities of s-cis and s-trans conformers have the same value for enones **7–9** (c and t) as for the other enones (eq 7) and that the ratio of the specific intensities of E and G conformers is a constant (eq 8). Rewriting eq 1 and 5–8 leads to eq 9 which gives a relatively poor fit with experimental results: r = 0.885, α = 0.7, $i_G{}^{\text{s-cis}}$ = 4300, $i_G{}^{\text{s-trans}}$ = 6900, $i_E{}^{\text{s-cis}}$ = 6100, and $i_E{}^{\text{s-trans}}$ = 9800. This imprecision is not surprising in view of the errors on each measurement (see Experimental Section).

However, eq 9 provides an order of magnitude for the different specific intensities and it is therefore possible to estimate the molar fractions of all the conformers (see Table V). As we have pointed out before,[13] the E and G conformations are not necessarily exactly as shown in Figure 4, but it is clear that enones **7–9** (c and t) are largely in the G conformation. For R = Pr and *i*-Bu (see Table IV) this conformer probably also occurs in the s-trans conformation, to a lesser extent, and it has no significant effect on $\nu_{C=C}$. The reason is probably that Pr and *i*-Bu do not have the three methyl groups β to the carbonyl, which is required to ensure that at least one of these be always in the neighborhood of the C=C bond.

$$I_G{}^{\text{s-trans}}/i_G{}^{\text{s-trans}} + I_E{}^{\text{s-trans}}/i_E{}^{\text{s-trans}} = x^{\text{s-trans}} \quad (5)$$

$$I_G{}^{\text{s-cis}}/i_G{}^{\text{s-cis}} + I_E{}^{\text{s-cis}}/i_E{}^{\text{s-cis}} = x^{\text{s-cis}} \quad (6)$$

$$i_G{}^{\text{s-trans}}/i_G{}^{\text{s-cis}} = i_E{}^{\text{s-trans}}/i_E{}^{\text{s-cis}} = 1.6 \quad (7)$$

$$i_G{}^{\text{s-trans}}/i_E{}^{\text{s-trans}} = i_G{}^{\text{s-cis}}/i_E{}^{\text{s-cis}} = \alpha \quad (8)$$

$$I_G{}^{\text{s-cis}} + I_G{}^{\text{s-trans}}/1.6 = -\alpha(I_E{}^{\text{s-cis}} + I_E{}^{\text{s-trans}}/1.6) + i_G{}^{\text{s-cis}} \quad (9)$$

Influence of the Conformation of R on Uv Spectra. The first important feature of the uv spectra of enones **7–9** (c and t) is that $\nu_{\pi\rightarrow\pi^*}$ has the same value for *trans*- (**9t**) and *cis*-*t*-Bu(Me)$_2$CCOCH=CHMe (**9c**), appreciably lower (800 cm^{-1}) than the wave number of other entirely s-cis enones (**6t** and **1–6c**). The ir spectral data show that the *t*-Bu(Me)$_2$C– group is gauche with respect to the carbonyl. We therefore propose that the proximity of the gauche *t*-Bu and the C=C bond is responsible for this bathochromic shift of $\nu_{\pi\rightarrow\pi^*}{}^{\text{s-cis}}$. A possible interpretation will be discussed below. This hypothesis may be generalized as follows. Each association of conformations gives a fixed $\nu_{\pi\rightarrow\pi^*}$: s-trans E, 47,500 cm^{-1}; s-trans G, 46,700 cm^{-1} (47,500 − 800 cm^{-1} if we assume that the effect of the *t*-Bu group is the same in the G conformation whether the enone is s-trans or s-cis); s-cis E, 45,100 cm^{-1}; s-cis G, 44,300 cm^{-1}. Since experimental values of $\epsilon_{\pi\rightarrow\pi^*}$ vary no more in this series than

---

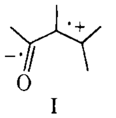
(26) M. Montagné, P. Arnaud, and P. Nounou, communication to the Organic Chemistry Days in Orsay (France), Société Chimique de France, Sept 1968.

in other ones, we may assume that they are equal for all the conformations. It is thus possible to perform a linear combination of these four bands, based on the molar fractions measured by ir spectroscopy. A simple algebraic calculation gives eq 10, which allows the determination of $\nu_{\pi\rightarrow\pi*}{}^{\text{calcd}}$ for enones **7** and **8** (c and t).

$$\nu_{\pi\rightarrow\pi^*}{}^{\text{calcd}} = 47{,}500 - 2400x - 800(x_6{}^{\text{s-trans}} + x_6{}^{\text{s-cis}} \quad (10)$$

Table II shows that the fit between calculated and experimental values is remarkably good, considering that the molar fractions are only rough estimates.

This fit is obtained on the assumption there is a special effect owing to the proximity of a Me group and the C=C bond. The nature of this effect is difficult to understand in detail. In a similar case, the special bathochromic shift created by two neoPe groups in the α-enone MeCOCH=C(neoPe)$_2$ [27] was explained by Arnaud, *et al.*,[26] in terms of three factors: angular opening of the bonds linking the ethylenic carbons to the neoPe groups; the inductive effect of these groups (in the sense of the electron displacement in the σ bonds); a "field effect" through space between the terminal Me groups of neoPe and C=C bond. It seems clear that the first two effects cannot influence $\nu_{\pi\rightarrow\pi^*}$ in our case, since R is attached to the carbonyl carbon. Assuming that this additional bathochromic shift is attributable to a field effect, we would tentatively propose the following explanation. If it is true that the $\pi \rightarrow \pi^*$ transition of α-enones involves transfer of the greater part of one electron between C=C and C=O bonds,[28,29] the $\pi \rightarrow \pi^*$ excited state will be of type I in which the ethylenic part of the molecule resembles the ionized state (by electron impact for example) of an olefin (II). It is well-known that these states lead to rearrangements[30] when one hydrogen atom is near the positive charge. We do not suggest that such a rearrangement occurs in the excited state of enones, but the assumption that the proximity of a Me group stabilizes the $\pi \rightarrow \pi^*$ excited state, giving rise to a bathochromic shift, is not unreasonable.



I

II

Conclusion

This work can be taken as evidence of two phenomena which have never been previously described: (a) $\nu^{\text{s-trans}}$ and $\nu^{\text{s-cis}}$ are constant whatever the configuration and regardless of the identity of R in RCOCH=CHMe; (b) there is a bathochromic shift of 800 cm^{-1} when there is a terminal Me group of R in the vicinity of the C=C bond. It would be important to take into account these points in any theoretical treatment of alkyl group effects on electronic spectra of conjugated systems. Woodward,[1] Fieser and Fieser,[31] or Evans and Gillam[32] have given very useful empirical formulations, but there are very few semiempirical calculations on such systems.

As a result of this work, it is now necessary to separate "conformational" and "electronic" effects of all groups R, R$_\alpha$, R$_{\beta c}$, and R$_{\beta t}$ bonded to the –COC=C framework. To this end, a method analogous to ours may be used for other conjugated systems. In the α-enal series, this would be easy since these compounds seem to be exclusively s-trans.[8] However, the uv results are not very reliable (for example, compare results from ref 6 and 33). In the α-diene series, conformational study seems to be more difficult than in the enones owing to the uncertainty about the conformation of some dienes (s-cis or nonplanar).[34,35]

Above all, in these two cases the number of different structures studied in the literature is not sufficient for a valid application of our method. Nevertheless, we come to the following conclusions regarding the enone series.

(a) Since the structural effect of R on $\nu_{\pi\rightarrow\pi^*}$ does not depend on the nature of R$_{\beta t}$, R$_{\beta t}$ cannot have any influence on the s-cis $\leftrightarrows$ s-trans equilibrium. This is understandable since there is no steric interference between R$_{\beta t}$ and R or the carbonyl (if steric crowding is the only relevant factor).

(b) Theoretical or semiempirical interpretations of the bathochromic shift of alkyl groups must take into account not only (conjugative or inductive) electronic effects but also a possible "field effect" between Me groups and the C=C bond.

(c) All the s-cis RCOCH=CHMe have the same $\nu_{\pi\rightarrow\pi^*}$. The electronic effect of a Me R$_{\beta c}$ or R$_{\beta t}$ is thus the same. It seems reasonable that it is true also for other alkyl groups. However, if R$_{\beta c}$ is a bulky group, it twists the molecule to a gauche s-cis conformation,[36,37] so giving an additional effect.

(d) The overall effect of substituting an H by a Me at R$_{\beta c}$ is the electronic effect plus the conformational effect. The latter is zero if R is a tertiary alkyl group (*e.g.*, *t*-Bu or Tm) since in this case the enones are always s-cis regardless of R$_{\beta c}$. The conformational effect is, however, not to be neglected if R is other than tertiary; if R = Me, for example, the molar fraction of the s-trans conformer is important (69%) in the trans isomer (R$_{\beta t}$ = Me, R$_{\beta c}$ = H) while it is zero in the cis isomer (R$_{\beta t}$ = H, R$_{\beta c}$ = Me).

(e) The "conformational" and "electronic" effects must occur when R$_\alpha$ is large, since the angle of twist in RCOC(R$_\alpha$) = CH$_2$ increases with the bulkiness of R and R$_\alpha$.[38]

Experimental Section

Ir spectra were obtained on a Perkin-Elmer Type 225 spectrometer with a 0.7-cm^{-1} spectral slit width and a scanning speed of 0.1 cm^{-1}/sec (1500–1800 cm^{-1}). The compounds were dissolved in hexane at 2–5 × 10^{-2} mol l.$^{-1}$. Cells were 1 mm thick with KBr windows. Spectra of solutions were compared with the solvent spectrum in

---

[27] P. Arnaud and M. Montagné, *C. R. Acad. Sci.*, **251**, 998 (1960).

[28] H. Suzuki in "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, London, 1967.

[29] J. N. Murrell, *J. Chem. Soc.*, 3779 (1956).

[30] F. W. McLafferty in "Spectroscopie de Masse," Ediscience, Paris, 1969.

[31] L. F. Fieser and M. Fieser in "Steroids," Reinhold, New York, N. Y., 1959.

[32] L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

[33] W. F. Forbes and R. Shilton, *J. Amer. Chem. Soc.*, **81**, 786 (1959).

[34] R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964).

[35] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, **87**, 3451 (1965).

[36] J. K. Groves and N. Jones, *Tetrahedron*, **25**, 223 (1969).

[37] D. D. Fauk and A. Fry, *J. Org. Chem.*, **35**, 364 (1970).

[38] A. Bienvenüe and B. Duchatellier, *Tetrahedron*, **28**, 833 (1972).

the same cell. Peak positions could be measured with a precision of ±1 cm^{-1}; the instrumental scale was checked frequently by means of the absorptions at 1710.2, 1704.5, 1690.15, 1671.5, and 1662.8 cm^{-1} of the water vapor spectra and was found to vary by less than 0.5 cm^{-1}. The absorbance *vs.* wave number curve presented two well-resolved clusters which were analyzed into Lorentzian components[39] by means of a Du Pont "curve resolver." The precision of the analysis varies with the number of components. In C=O or C=C systems with only two components, we obtain an unambiguous and very precise solution (mean deviation between experimental and calculated curves is lower than 0.01 absorbance unit; maximum deviation is 0.02 absorbance unit). The area of the Lorentzian curves is 1.57 $\epsilon_{\max}W_{1/2}$ with a precision of about ±5% for strong bands and about ±10 to ±30% for weak bands, after 5 runs. In systems with more than two components, there is no unique solution. However, by assuming that all the curves have $W_{1/2}$ of the same order, five runs give the areas to ±10% precision on strong bands and to between ±20 to ±50% on the weaker bands. The precision on the wave numbers at maximum absorbancy is ∓1 cm^{-1} in the first case and ±3 cm^{-1} in the second case. The absolute error on the molar fractions of different conformers is about 0.05.

Uv spectra were recorded on a Cary Model 15 spectrophotometer (1-mm cell) in hexane at concentrations ranging from 5×10^{-4} to 10^{-3} mol l.$^{-1}$. The $\nu_{\max}$ wave numbers were accurate to ±50 cm^{-1}, and the molecular absorption coefficient $\epsilon_{\max}$ is accurate to ±5%. The half-height width $W_{1/2}$ and the half-height dissymmetry (Dis) are accurate to ±100 cm^{-1} and ±200 cm^{-1}, respectively. The larger part of the $\pi \rightarrow \pi^*$ band was always at the higher frequencies. These two last measurements were certainly marred by a systematic error owing to the beginning of a new transition at the higher wave numbers.

Preparation of Trans Enones. 3-Penten-2-one (1) was prepared following the previously described method.[40]

3-Hexen-2-one (2) was prepared following Normant's method by condensation of the Grignard reagent of 1-bromo-1-propene with propionic anhydride (−80° in THF).[41,42]

Other trans enones (3–9) were obtained, generally without their cis isomers, by dehydration of the corresponding β-hydroxy ketones (see preparation below). A mixture of the β-hydroxy ketone with 10% of oxalic acid and the quantity of benzene required for a boiling point of about 90° was refluxed 2–3 hr in a Dean–Stark apparatus. When the evolution of water ceased, the reaction mixture was washed with dilute aqueous sodium bicarbonate solution and with water, and the organic layer was dried on $MgSO_4$. On fractionation, crude products were obtained (see Table VI).

Table VI. Fractionation of Trans Enones

Enone no.	% yield[a]	Bp, °C (mm)	% pure trans enone[b]
3t	85	58–70 (25)	75
4t	85	51–65 (15)	95
5t	78	40–65 (30)	90
6t	98		75
7t	89	66–85 (15)	87
8t	85	60–71 (5)	80
9t	92	55–56 (2)	80

[a] From quantity of pure trans enone. [b] From vpc, in the fraction.

Preparation of β-Hydroxy Ketones $RCOCH_2CHOHMe$ (R = Pr, 3a; R = *i*-Bu, 4a; R = *i*-Pr, 5a; R = *t*-Bu, 6a; R = neoPe, 7a). These compounds were obtained by ketolization of the appropriate saturated ketone and ethanal in basic medium following the procedure of Dubois and Dubois.[43] Yields (from quantities of β-hydroxy ketones and enones measured by vpc) were respectively (in %): 35, 30, 30, 26, and 45 for compounds **3a** to **7a**.

Preparation of β-Hydroxy Ketones $RCOCH_2CHOHMe$ (R = CH(Me)-*t*-Bu, 8a; R = Tm, 9a). The above method does not give good yields in this case, so the saturated ketone was enolized with *i*-PrMgCl before condensation with ethanal. The saturated ketone (0.2 mol) diluted in 50 ml of anhydrous ether was added to *i*-PrMgCl (0.2 mol, 2 *N* in ether), giving a thick white mixture. During 0.5 hr, 0.2 mol of ethanal (freshly distilled) diluted in 15 ml of anhydrous ether was added, the temperature being maintained below 15°. The mixture was hydrolyzed on crushed ice and extracted three times with ether. The ethered layers, after washing with water, were dried on K_2CO_3, then on $MgSO_4$. After evaporation of the ether, a crude product was obtained with yields of 65 and 60% respectively for **8a** and **9a**.

The saturated ketones used in this synthesis were $MeCOC(Me)_2$-*t*-Bu[44] and MeCOCH(Me)-*t*-Bu, the preparation of which is described below.

Preparation of 3,4,4-Trimethylpentan-2-one (8b). The synthesis by the well-known Grignard method[45] is inconvenient because *t*-Bu(Me)CHCOCl and especially *t*-Bu(Me)CHCl[46,47] are very difficult to obtain. Another approach would be the hydrogenation of 3-*tert*-butyl-3-buten-2-one, obtained by Mannich synthesis on methyl neopentyl ketone.[48] However, apart from the fact that the experimental procedure of this preparation was not specified, the condensation seems to take place on the Me group bonded to the carbonyl.[49] The following scheme was therefore adopted

$$\text{MeCOCOMe} + t\text{-BuMgCl} \longrightarrow \underset{\mathbf{8e}}{t\text{-BuC(Me)(OH)COMe}} \xrightarrow[\text{2. pyrolysis}]{\text{1. Ac}_2\text{O}}$$

$$\underset{\mathbf{8c}}{\text{CH}_2\text{=C(}t\text{-Bu)COMe}} \xrightarrow{+\text{H}_2} \mathbf{8b}$$

3,4,4-Trimethylpentan-3-ol-2-one (8e) was prepared by condensation of biacetyl with *t*-BuMgCl. The Grignard compound was prepared under argon from 94 g (1.05 mol) of *t*-BuCl and 1 g-atom of doubly sublimed Mg in 600 ml of anhydrous ether (90% yield). Biacetyl (232 g, 2.7 mol), diluted in 650 ml of anhydrous ether, was cooled to −30° in a three-necked flask fitted with a condenser and a mechanical stirrer. The decanted Grignard (550 ml, 0.82 mol) was added dropwise in 5.5 hr after which the mixture was kept 1 hr at −30°. Hydrolysis was effected in the cool flask with 33 ml of concentrated HCl in 50 ml of water. The ether extract was washed in turn with concentrated aqueous sodium bicarbonate solution and a saturated NaCl solution. The organic layer was dried with $MgSO_4$ and concentrated. Vacuum distillation gave 51.6 g of **8e** (80% pure, 40% yield in pure product): bp 57° (7 mm); nmr 1.22 (s, 9 H), 1.52 (s, 3 H), 2.52 (s, 3 H), 4.52 (s, 1 H).

Dehydration of 8e. In the first step the hydroxy group was acetylated by Oppenauer's method.[50] LiH (4.8 g, 0.53 mol) and 240 g (2.36 mol) of freshly distilled acetic anhydride (bp 138°) were refluxed for 1 hr in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. Then, 84.8 g (0.59 mol) of pure (**8e**) was added, and the mixture was refluxed at 136–138° for 4 days. After the mixture was cooled, it was poured carefully onto ice and stirred for 2 hr. The resulting black liquid was neutralized, filtered, and extracted four times with ether. The ether extract was dried on $MgSO_4$. The **8d** product (89% yield) was obtained in two fractions: bp 61–66° (4 mm), 30.4 g (76% pure), and bp 66–71° (4 mm), 67.6 g (97% pure). The pyrolysis of the acetate (**8d**)[51] furnished the enone (**8c**). The pyrolysis was performed in a 1-cm i.d. Pyrex tube filled with "Dexion Gauze rings" and heated to 500° (temperature controlled between 497 and 511°). The product was gently flushed with nitrogen. Some of the product (**8d**) (30 g) was added dropwise in 5.5 hr, then the reaction products were

---

(39) R. P. Young and R. N. Jones, *Chem. Rev.*, 71, 219 (1971).

(40) J. E. Dubois and C. Moulineau, *Bull. Soc. Chim. Fr.*, 2198 (1965).

(41) H. Normant in "Advances in Organic Chemistry: Methods and Results," Vol. 2, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience, New York, N. Y., 1960.

(42) G. Martin, *Ann. Chim. (Paris)*, 541 (1959).

(43) J. E. Dubois and M. Dubois, *Bull. Soc. Chim. Fr.*, 3120 (1969).

(44) J. E. Dubois and P. Bauer, *Bull. Soc. Chim. Fr.*, 1156 (1967).

(45) J. E. Dubois, M. Chastrette, and C. Letoquart, *C.R. Acad. Sci.*, **264**, 1124 (1967); J. E. Dubois, B. Leheup, F. Hennequin, and P. Bauer, *Bull. Soc. Chim. Fr.*, 1150 (1967); J. E. Dubois, M. Boussu, and C. Lion, *Tetrahedron Lett.*, 829 (1971).

(46) J. E. Dubois and M. Boussu, *C. R. Acad. Sci., Ser. C*, **268**, 1603 (1969).

(47) M. S. Newmann, A. Arkell, and T. Fukunaga, *J. Amer. Chem. Soc.*, **82**, 2498 (1960).

(48) R. Heilmann, G. De Gaudemaris, and P. Arnaud, *C. R. Acad. Sci.*, 234, 1177 (1952).

(49) T. A. Spencer, D. S. Watt, and R. J. Friary, *J. Org. Chem.*, **32**, 1234 (1967).

(50) R. V. Oppenauer, *Monatsh. Chem.*, **97**, 162 (1966).

(51) H. Gudgeon, R. Hill, and E. Isaacs, *J. Chem. Soc.*, 1926 (1951).

rinsed with 50 ml of hexane. The mixture obtained was washed with saturated aqueous Na_2CO_3 solution and with water and was dried on $MgSO_4$. Enone **8c** (12.5 g) (98% pure, 61% yield) was obtained, bp 57° (40 mm); nmr 1.12 (s, 9 H), 2.24 (s, 3 H), 5.66 (s, 1 H), 5.75 (s, 1 H).

3,4,4-Trimethylpentan-2-one (8b) was obtained by catalytic (Raney Ni) hydrogenation of **8c** in absolute EtOH at about 30° under atmospheric pressure (80% yield).

Preparation of Cis Enones (10–18). All cis enones were prepared by fractionation of the acidified trans enones; the following synthesis is typical. Enone **7** (9.5 g) and 0.1 g of paratoluenesulfonic acid were distilled (15 mm) with a reflux ratio of 100:1 on a 25 theoretical plate spinning band column (see Table VII).

Table VII

Fraction no.	Bp, °C	Weight, g	% trans enone	% cis enone
1	58–63	1.0	69	28
2	63–60	1.6	42	57
3	60–58	1.2	26	73
4	58	1.5	41	58
Residue		4.5		

It was impossible to obtain pure cis enone directly; fractions 2–4 of this example were purified by preparative vpc.

Purification of Enones. All enones were purified on Aerograph Autoprep vpc apparatus with a 10 ft, 15% SE30 on 100–120 Chromosorb W column. With one exception (see Table II) products were purer than 99%, as checked using a Aerograph Model 1200 chromatograph, just before and after obtaining spectra. This precaution was very important, above all for cis enones which isomerize quickly (giving trans enones and other unidentified products) under the influence of light.

Product Identification. In addition to uv (observed n → π* bands have not been noted in this paper) and ir spectra (see Tables II and III) which are very typical of the –COC=C framework, nmr spectra were recorded (about 10% in CCl_4) on a Varian Model DP60 and a JEOL Model JNM C60 HL (see Table VIII).

Table VIII. Nmr Spectra for Trans and Cis Enones[a]

Enone no.	δ_R	δ_{Me}[b]	Enone no.	δ_R	δ_{Me}[b]
2t	2.42 (2 H)m 1.05 (3 H)t	2.10	**2c**	2.45 (2 H)m 1.05 (3 H)t	1.80
3t	. . .[c]	2.07	**3c**	. . .[c]	1.84
4t	. . .[c]	2.06	**4c**	. . .[c]	1.86
5t	2.84 (1 H)m 1.07 (6 H)d	2.08	**5c**	2.70 (1 H)m 1.06 (6 H)d	1.90
6t	1.12 (9 H)s	2.06	**6c**	1.12 (9 H)s	1.88
7t	1.00 (9 H)s 2.26 (2 H)s	2.08	**7c**	1.00 (9 H)s 2.30 (2 H)s	1.87
8t	0.91 (9 H)s 0.98 (3 H)d 2.50 (1 H)m	2.10	**8c**	0.91 (9 H)s 0.98 (3 H)d 2.50 (1 H)m	1.89
9t	0.90 (9 H)s 1.08 (6 H)s	2.03	**9c**	0.90 (9 H)s 1.09 (6 H)s	1.87

[a] δ for ethylenic protons are not given since this portion of the spectrum was not analyzed. For trans enones, ten peaks corresponding to an ABX_3 spectrum with J = 15–17 Hz, between about 6 and 7 ppm, were observed. For cis enones, it seems that the δ of the two ethylenic protons are very similar. For enones **1t** and **c** see E. S. Waight and R. L. Erskine in "Steric Effects in Conjugated Systems," Butterworths, London, 1958. [b] δ of the center of the doublet. [c] Multiplets.

The value of δ_{Me} in cis and trans enones is in agreement with Baldwin's results[9] for 3-penten-2-one.

Acknowledgment. We wish to acknowledge our indebtedness to Professor J. E. Dubois for helpful discussions, to Professor J. P. Matthieu who allowed us access to his "curve resolver" and to Mrs. B. Duchatellier for invaluable help with the synthesis.

Substituent Effects. XI.[1] Polar and π-Electron Substituent Effects by ^{19}F Nuclear Magnetic Resonance

W. Adcock, M. J. S. Dewar,*[2] and B. D. Gupta

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, and the School of Physical Sciences, The Flinders University of South Australia, Bedford Park, S.A. 5042 Australia.

Received April 27, 1973

Abstract: A number of substituted aryl fluorides have been synthesized and their ^{19}F chemical shifts measured. The results provide conclusive experimental proof that polar effects play a major role in determining ^{19}F chemical shifts in aryl fluorides. Furthermore, the ^{19}F chemical shifts provide definitive experimental evidence for hyperconjugative electron withdrawal by substituted methyl groups in the ground state of neutral molecules.

The large response of ^{19}F chemical shifts to substituent-produced perturbations has made fluorine nuclear magnetic resonance spectroscopy an attractive tool for the study of substituent effects.

Since the fluorine chemical shifts are dominated by the paramagnetic term of the Ramsey equation,[3] certain approximations are usually unavoidable if they are to be discussed in the terms that have proved useful in the case of chemical reactivity.[4] A number of theo-

---

(1) Part X: M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Amer. Chem. Soc.*, **93**, 4187 (1971).

(2) To whom correspondence should be addressed at The University of Texas at Austin.

(3) (a) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954); (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965, Chapter 4.

(4) M. Karplus and T. Das, *J. Chem. Phys.*, **34**, 1683 (1961).