The Influence of Conformation on Transmission of Electronic Effects in α,β-Unsaturated Ketones

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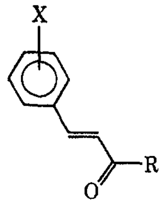
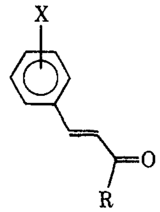
Only recently has the influence of conformation on transmission of electronic effects in α,β-unsaturated ketone systems been investigated. Perjéssy,[2] in a thorough investigation of substituent effects on the infrared stretching frequencies of chalcones, has concluded that s-trans conformers transmit more effectively than s-cis conformers on the basis of the magnitude of Hammett ρ values obtained when $\nu_{C=O}$ was plotted against σ^+. In the same report,[2] data previously reported by Dimmock,[3] *et al.*, for butyl styryl ketones were interpreted in a similar manner.

The previous investigations of transmission by s-cis–s-trans conformers of α,β-unsaturated ketones (Ia,b)



(s-cis)



(s-trans)

Ia, R = *n*-Bu
b, R = C_6H_5
c, R = H
d, R = CH_3

had as R groups *n*-butyl and phenyl groups which have rather large steric requirements. It seems likely that a significant amount of the difference in transmission of effects between s-cis and s-trans isomers for Ia and Ib may arise from differences in coplanarity of the two isomers. For example, examination of Drieding models indicates that in the case of the s-cis isomer of Ia and Ib the R group and the α hydrogen are in close proximity and their interaction should alter the coplanarity of the styryl group and the carbonyl group. If the R group were smaller, there should be less interaction between it and the α hydrogen and hence it would be possible for a greater degree of coplanarity to be achieved. It might be expected that the transmission of electronic effects in the two conformations should become very nearly the same when the steric interaction of R and the vinyl hydrogens is reduced, if the degree of coplanarity of the styryl group and carbonyl group is important for transmission of electronic effects. The case Ic, in which R = H, should have minimum steric interactions; however, the conformational isomers of cinnamaldehyde cannot be detected by infrared spectroscopy.[4] Consequently, we have selected the system Id, methyl styryl ketones, R = CH_3, for study.

Although the steric requirements of the methyl group are considerable, they are significantly less than those of the *n*-butyl and phenyl groups which were used as R in the previous studies. When R is methyl (Id), there is a smaller interaction with the α hydrogen in the s-cis conformer; hence, if the degree of coplanarity is important to the efficiency of transmission, then a study of the methyl styryl ketone system should provide insight into its role. To test this point and as a part of our continuing investigation[5] of structure–reactivity relationships of α,β-unsaturated ketones, we have measured the carbonyl stretching frequencies of the s-cis and s-trans conformers of a series of substituted methyl styryl ketones.

Hayes and Timmons[4] have previously reported the assignment of the bands in the 1690-cm^{-1} region to the s-cis or nonplanar conformer and the bands in the 1670-cm^{-1} region to the s-trans conformers for 2 and 4. The assignments reported here are based on analogy with their work. As anticipated, the lowest carbonyl frequencies were obtained for Id substituted with the strongest electron-withdrawing group and the highest frequencies were observed for Id substituted with the strongest electron donating group.

The methyl styryl ketones employed in this investigation are listed in Table I along with the values for carbonyl stretching frrquencies which were obtained in carbon tetrachloride solution. The frequencies for both conformers are correlated with σ^+ obtained from the tabulation of Ritchie and Sager.[6] Table II contains the results of the statistical analysis[7] of the correlations carried out according to the approach of Jaffé.[8] Figure 1 contains a graphical presentation of

TABLE I
METHYL STYRYL KETONES

Compd no.	Substituent	$\nu_{\text{s-cis}}$, cm^{-1}	$\nu_{\text{s-trans}}$, cm^{-1}
1	*p*-$(CH_3)_2N$	1688.9	1666.0
2	*p*-CH_3O	1693.2	1670.1
3	*p*-C_6H_5	1696.9	1674.0
4	*p*-H	1697.6	1674.8
5	*p*-Cl	1699.2	1677.2
6	*p*-Br	1699.3	1678.3
7	*p*-CN	1701.1	1680.0
8	*p*-NO_2	1702.0	1680.8

TABLE II
RESULTS OF STATISTICAL TREATMENT USING σ^+ CONSTANTS[a,b]

	n	ρ	*s*	*i*	*c*
s-cis-Id	8	5.38	0.48	1697.9	0.995
s-trans-Id	8	6.22	0.98	1675.9	0.984

[a] See ref 6. [b] *n* = number of points; ρ = slope as determined by method of least squares; *s* = standard deviation; *c* = correlation coefficient; *i* = intercept.

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[1] American Chemical Society–Petroleum Research Fund Scholar.

[2] A. Perjéssy, *Chem. Zvesti*, **23**, 905 (1969).

[3] J. R. Dimmock, P. L. Carter, and P. D. Ralph, *J. Chem. Soc. B*, 698 (1968).

[4] W. P. Hayes and C. J. Timmons, *Spectrochim. Acta.*, **24A**, 323 (1968).

[5] (a) N. S. Silver and D. W. Boykin, Jr., *J. Org. Chem.*, **35**, 759 (1970); (b) R. W. Woodard and D. W. Boykin, Jr., *Chem. Commun.*, 628 (1970); (c) M. L. Ash, F. L. O'Brien, and D. W. Boykin, Jr., *J. Org. Chem.*, in press.

[6] C. D. Ritchie and W. F. Sager in "Progress in Physical Organic Chemistry," Vol. 2, Interscience, New York, N. Y., 1964.

[7] G. W. Snedecor and W. G. Cochran, "Statistical Methods," 6th ed, Iowa State University Press, Ames, Iowa, 1967.

[8] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

TABLE III

RESULTS OF STATISTICAL TREATMENT USING F AND R CONSTANTS[a,e]

	n	f	r	i	E	c	% R
s-*cis*-Ia	5[b]	7.65 ± 0.78	16.14 ± 1.51	1694.9	0.53	0.994	46 ± 3
s-*trans*-Ia	5[b]	14.24 ± 1.47	29.72 ± 2.86	1675.0	1.0	0.994	46 ± 3
s-*cis*-Ib	9[c]	4.88 ± 1.26	6.24 ± 1.83	1672.2	1.30	0.945	40 ± 9
s-*trans*-Ib	9[c]	5.32 ± 1.52	10.86 ± 2.21	1653.0	1.57	0.959	56 ± 9
s-*cis*-Id	7[d]	3.27 ± 1.12	8.94 ± 1.90	1697.4	1.01	0.960	59 ± 10
s-*trans*-Id	7[d]	4.98 ± 1.54	10.16 ± 2.62	1674.5	1.39	0.953	52 ± 10

[a] Swain–Lupton field and resonance parameters; see ref 9. These correlations were made using a multiple linear regression program written using the statistical analysis described in ref 7. Calculations were made on an IBM 7094 computer. [b] The ν values were taken from ref 3; the substituents were p-H, p-Cl, m-Cl, p-CH_3, and p-CH_3O. [c] The ν values were taken from ref 2; the substituents were p-NH_2, p-CH_3O, p-CH_3, p-H, p-F, p-Cl, m-Cl, p-CN, p-NO_2. [d] The value of ν for the p-$(CH_3)_2N$ compound was not used in these calculations. [e] n = number of points; f = regression coefficient for field parameter; r = regression coefficient for resonance parameter; i = intercept; E = standard error of estimate; c = multiple correlation coefficient; % R = resonance contribution, calculations as in ref 5a.

the data. The correlations of the stretching frequencies with σ^+ are good for both isomers, for the s-cis $r = 0.995$ and, for s-trans, $r = 0.984$.

Comparison of ρ values for the two conformers of the methyl styryl ketones indicates that their abilities to transmit electronic effects are very similar. The ratio ρ-cis/ρ-trans is 0.86 for the methyl styryl ketones. This value is an increase over the values of the s-cis–s-trans of 0.76 and 0.78 for R = n-Bu and $-C_6H_5$ (Ia and Ib), respectively.[2] While the ratio does not reach unity, it is in good agreement with the value of 0.90 for the ratio reported for a series of 4′-substituted chalcones.[2] These results are in accord with the hypothesis that, as the two conformers approach similar degrees of coplanarity, their abilities to transmit electronic effects become similar.

The above results suggest that an important mode of transmission of electronic effects in these systems is by resonance. The linear free energy relationship reported by Swain and Lupton[9] provides a method by which the contribution of resonance to a correlation may be assessed. Table III contains the results of the correlations of the stretching frequency data for Ia, Ib, and Id with the Swain–Lupton expression. As has been noted previously[5a] for ir data, correlations with the two-parameter expression are generally poorer than those obtained with the Hammett expression. In general, and not unexpectedly, all systems give values for % R which are approximately the same. Unfortunately, the correlations are such that the error in the % R calculations is so high for Ib and Id that it is not possible to draw conclusions about trends. In order to rigorously determine the effect of conformation on the mode of transmission in these α,β-unsaturated systems, it will be necessary to find another more precise means of assessing them.

Experimental Section

Methyl Styryl Ketones.—All of the ketones have been previously reported and were prepared as described by Johnston and Jones.[10] The compounds were purified by recrystallization, usually from hexane and their purity was checked by nmr. The compounds were dried *in vacuo* prior to measurement of their stretching frequency. Melting points are uncorrected and were obtained using a Thomas-Hoover Uni-Melt. The melting points observed followed by the literature values follow:

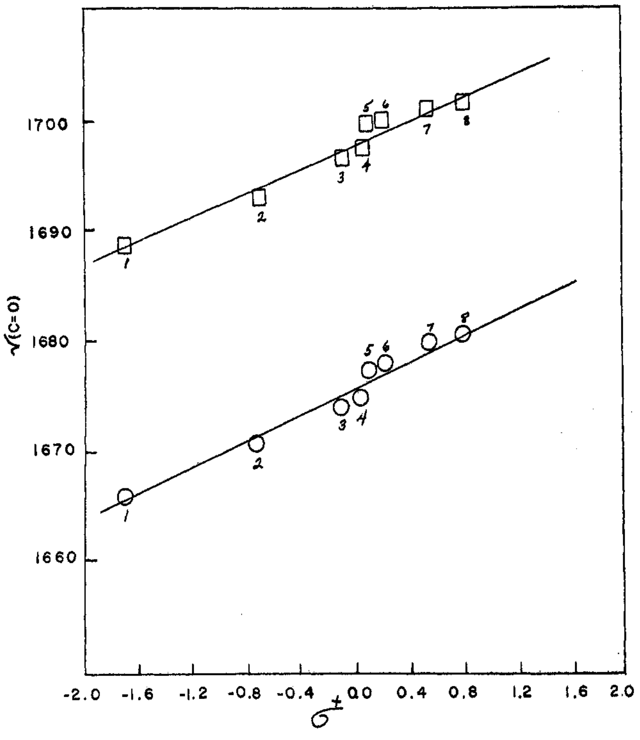

Figure 1.—Plots of $\nu_{C=O}$ *vs.* σ^+ for s-cis and s-trans conformers of para-substituted benzalacetones: □, s-cis conformers; ○, s-trans conformers.

1, 135.5–136.5° (133–134°);[10] **2**, 72–73° (72°);[11] **3**, 134–135° (134.5°);[12] **4**, 40–41° (40–41°);[10] **5**, 58–59° (58–59°);[10] **6**, 84.5–85.0° (83–84°);[13] **7**, 105–106.5° (105–106°);[10] **8**, 108–109° (106–107°).[10]

Infrared Frequencies.—The ir stretching frequencies for all the benzalacetones were determined using a Beckman IR-12 grating spectrometer operated in the expanded scale mode at scan rates of 8 cm^{-1} min, chart speeds of 1 in./min, and period setting of 8.[5a] The spectra of the benzalacetones were taken in solutions of spectral grade carbon tetrachloride at 35 ± 4°. The concentrations of the solutions were *ca.* 5% and a matched set of KBr cells with 0.05-mm path lengths were used. Band frequencies were taken at the half-width at 75% of the height of the s-cis band and at the half-width at 60% of the height of the s-trans band. All frequencies reported were obtained from averaging at least three different scans, all of which gave frequencies which were within 0.4 cm^{-1} of one another.

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[9] C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

[10] R. L. Johnston and L. A. Jones, *J. Chem. Eng. Data*, **16**, 112 (1971).

[11] Kalle A.-G., British Patent 943,266 (1963); *Chem. Abstr.*, **60**, 14697*a* (1964).

[12] R. Trave and G. Bianchetti, *Atti. Accad. Naz. Lincei, Cl Sci. Fis., Mat. Nat. Rend.*, **11**, 211 (1951); *Chem. Abstr.*, **49**, 2381*h* (1955).

[13] R. E. Lutz, T. A. Martin, J. F. Codington, T. M. Amacker, R. K. Allison, N. H. Leake, R. J. Rowlett, Jr., D. Smith, and J. W. Wilson, III, *J. Org. Chem.*, **14**, 982 (1949).

Registry No.—**1**, 30625-58-2; **2**, 3815-30-3; **3**, 32979-83-2; **4**, 1896-62-4; **5**, 30626-03-0; **6**, 3815-31-4; **7**, 30626-00-7; **8**, 30625-98-0.

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[4,5-*c*(*d*)]Pyrazolotropone. A New Aromatic Ring System

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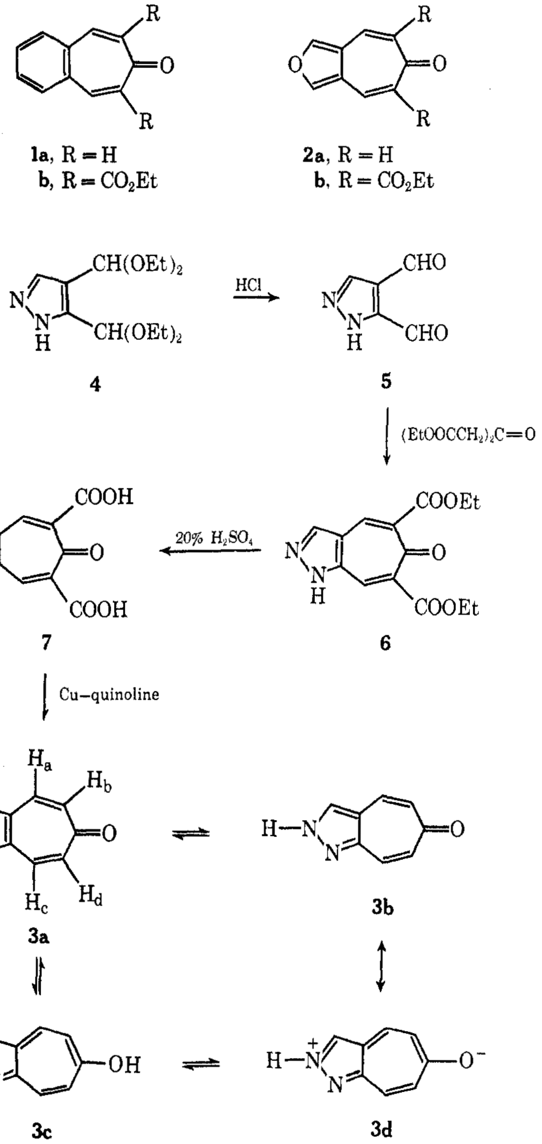
Heterocyclic analogs of 4,5-benzotropone (**1a**) were unknown until the recent preparations of 2-thiaazulen-6-ones,[2,3] 2-phenyl-1,3,5,7-tetramethyl-2-azaazulen-6-one,[3] and [4,5-*c*]furotropone (**2a**).[4] A hitherto unknown member of this series is [4,5-*c*(*d*)]pyrazolotropone (or 1,2-diaza-1*H*-azulen-6-one) (**3**), which could exist in any of several tautomeric structures **3a–d** (Scheme I). It was of interest to determine if the difference in basicity of the carbonyl group and the annular nitrogens would be relinquished for the stabilization which would result from further delocalization of the ten π electrons in the tautomer, 6-hydroxy-1,2-diazaazulene (**3c**).

A good yield of 2,7-dicarbethoxy[4,5-*c*(*d*)]pyrazolotropone (**6**)[5] was obtained as outlined in Scheme I. Its infrared spectrum (KBr) showed a broad band at 3226 cm^{-1} for the associated NH group in the pyrazole ring. The tropone ring carbonyl absorption was assigned to both bands at 1600 and 1520 cm^{-1} based on comparable bands reported[4] for the furotropone **2b** (1614 cm^{-1} in CH_2Cl_2) and the benzotropone **1b** (1625 and 1550 cm^{-1} in CH_2Cl_2). However, the intense band at 1600 cm^{-1} characteristic of the C=N absorption in pyrazoles[6] makes it difficult to definitely assign this band specifically as the carbonyl stretching frequency in **6**.

The ultraviolet absorption (methanol) at 222 nm (log ϵ 4.24) was attributed to the pyrazole ring, since alkyl-substituted pyrazoles absorb at 210–225 nm and arylpyrazoles at 250–280 nm.[6] The bands associated with the tropone ring (in isooctane at 225, 297, and 310 nm for tropone itself)[7] were shifted by the fused pyrazole chromophoric ring to 262 nm (log ϵ 4.43) and 316 (3.98), the latter band assigned to the conjugated keto function. Comparable absorptions were reported[4] for **2b**: $\lambda_{\max}^{\mathrm{EtOH}}$ 219 nm (log ϵ 4.14) and 260 (4.49). The nmr spectra of **1**, **2**,[4] and **6** (*cf.* Experimental Section) were also very similar with respect to chemical shift values and absorption patterns for the tropone rings.

SCHEME I



Hydrolysis of **6** with 20% sulfuric acid gave 2,7-dicarboxy[4,5-*c*(*d*)]pyrazolotropone (**7**) in 87% yield. The parent structure was then obtained in 35% yield by decarboxylation of **7** at 205° with a copper–quinoline mixture. This represents a different, convenient, and improved method for decarboxylation of the precursor dicarboxylic acids to yield tropones. Usually acid hydrolysis in sealed tubes affords very low yields.[4]

The extent of aromaticity in **3** was estimated by a comparison of some spectral characteristics with the data available on the related unsubstituted systems, **1a** and **2a**. The bands at 1635 and 1582 cm^{-1} in the infrared spectra of tropones were previously considered carbonyl group vibrations. A study[8] on a number of tropones revealed that the lower frequency band was solvent dependent and therefore it was concluded that

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[1] Taken from the Ph.D. dissertation of M. Pesce, St. John's University, June 1971.

[2] M. Winn and F. G. Bordwell, *J. Org. Chem.*, **32**, 1610 (1967).

[3] (a) A. V. El'tsov, A. A. Guinesina, and L. N. Kivokurtseva, *Zh. Org. Khim.*, **3**, 1343 (1967); *Chem. Abstr.*, **66**, 94581 (1967); (b) A. V. El'tsov, L. N. Kivokurtseva, and A. A. Guinesina, *Zh. Org. Khim.*, **4**, 907 (1968); *Chem. Abstr.*, **69**, 18958 (1968); (c) A. V. El'tsov, A. S. Guinesina, and L. N. Kivokurtseva, *Tetrahedron Lett.*, 735 (1968).

[4] M. S. Cook and E. J. Forbes, *Tetrahedron*, **24**, 4501 (1968).

[5] The nomenclature employed is analogous to that accepted for benzotropone and [4,5-*c*]furotropone,[4] the letters *c* and *d* referring to the numbering of the pyrazole ring in **3a** and **3b**, the numbers 4,5 referring to the side of the tropone ring fused to the pyrazole ring.

[6] A. N. Kost and I. I. Grandberg, "Advances in Heterocyclic Chemistry, Vol. 6, A. R. Katritzky and A. J. Boulton, Ed., Academic Press, New York, N. Y., 1966, pp 355–358, and references cited therein.

[7] W. von E. Doering and F. L. Detert, *J. Amer. Chem. Soc.*, **73**, 876 (1951).

[8] H. Goetz, E. Heilbronner, A. R. Katritzky, and R. A. Jones, *Helv. Chim. Acta*, **40**, 957 (1957).