ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM PASTORE CHEMICAL LABORATORY, UNIVERSITY OF RHODE ISLAND]

The Ultraviolet Absorption Spectra of Certain Aryl Ketones, Principally Benzylacetones

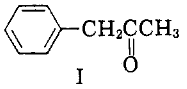
BY SAMUEL F. MARSOCCI AND SCOTT MACKENZIE

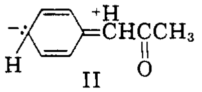
RECEIVED DECEMBER 15, 1958

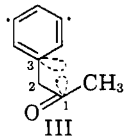
The increase in ketonic ϵ_{max} caused by the introduction of aromatic groups n CH_2's removed from the carbonyl group has been well described previously, particularly for compounds wherein $n = 1$. An effort is now made to correlate cases wherein $n = 2$. The success which has resulted favors a bond orbital overlap theory previously proposed.

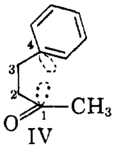
For some years it has been recognized[1-4] that α-phenylketones show an unusually intense absorption band in their ultraviolet spectra at about 290 mμ. Comparison of the spectral value of phenylacetone (I) (285 mμ, ε 150; EtOH)[1] with that of acetone (272.5 mμ, ε = 18.6; EtOH)[5] illustrates this great increase in the intensity of absorption.

An early explanation for this effect involved hyperconjugative action (II) through the methylene group.[1,6,7] However, Cookson,[4] in summarizing these effects, recently proposed another interpretation[8] which involved as a necessary condition the coplanarity of the p-orbitals of C_1 and C_3 (as in phenylacetone, III). This interpretation appears to suggest that the intervening carbon atoms do not play an important electronic role but merely regulate geometry. This in turn suggests that values for ϵ_{max} for various ketones can be estimated with the simplest sort of probability arithmetic. It is the purpose of the present work to examine certain ketones, principally benzylacetones, to see if the spectral values for these can be correlated using Cookson's suggestion.


I


II


III


IV

Experimental

All spectra which are reported herein were obtained using a Beckman DU spectrophotometer. Readings were taken every mμ near maxima; no effort was made to read at fractional parts of the mμ. Solutions of ketones were made up, solubility permitting, to a concentration of 10^{-1} M, this being diluted to 10^{-x} (where x is a whole number), as required. A single calibrated pipet was used throughout. Solvents, while not of purchased spectro-grade, were purified as previously described.

The following ketones were purified by distillation only: ethyl α-benzyl-α-propionylpropionate,[9] methoxyacetone,[10] methyl isobutyl ketone and cyclohexanone. Others were solids and purification presented no special problems: camphor, 1,1-diphenyl-2-propanone,[11] *p*-dimethylaminobenzalacetone,[12] *p*-dimethylaminobenzylacetone[12] and *p*-dimethylaminobenzhydrylacetone.[12] Still others, being liquids and of particular importance in the present work, were purified by recrystallization of the semicarbazones, the latter then being boiled with excess aqueous pyruvic acid to regenerate the ketones: furfurylacetone,[13] 2-furylacetone,[14] phenylacetone,[1] benzylacetone[15] and cinnamylacetone.[16]

Discussion

An attempt at making a correlation of spectral values of ketones with proximity interaction due to aryl groups requires consideration of both probability and geometry factors; the former will be dealt with first. If in phenylacetone (III) both the phenyl group and the acetyl group are assumed to be free rotors and $1/x$ is assumed to be the fraction of molecules (or the fraction of time for a given molecule) in which one of the p-orbitals of C_1 is in the plane of C_1–C_2–C_3, then $\epsilon_p = k/x^2$, k being a constant and ϵ_p being the increment of ε due to proximity effect. Implicit in this treatment is the suggestion that the total value of ε of phenylacetone is the sum of ϵ_p and ϵ_k, the latter being the contribution of molecules not engaged in proximity interaction. For benzylacetone (IV), the additional rotation of the C_2–C_3 bond must be accounted for so the value of ϵ_p becomes $k/2x^3$; the value for 1,1-diphenyl-2-propanone or 1,3-diphenyl-2-propanone, $2k/x^2$; for benzhydrylacetone, k/x^3; for 2-phenyl-1-cycloalkanones, k/x; and for totally rigid, bicyclo ketones with an interacted benzo group, k.

---

(1) W. D. Kumler, L. A. Strait and E. L. Alpen, THIS JOURNAL, **72**, 1463, 4558 (1950); A. C. Huitric and W. D. Kumler, *ibid.*, **78**, 614, 1147 (1956).

(2) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952).

(3) W. B. Bennett and A. Burger, *ibid.*, **75**, 84 (1953).

(4) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

(5) F. O. Rice, THIS JOURNAL, **42**, 727 (1920).

(6) E. A. Braude, *J. Chem. Soc.*, 1902 (1949), reviewed the interaction of non-conjugated chromophores.

(7) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, London, 2nd ed., 1957, p. 255.

(8) Used by P. D. Bartlett and B. E. Tate, THIS JOURNAL, **78**, 2473 (1956), to explain the abnormal spectrum of a bicycloölefinic ketone, and by P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1007 (1950), in connection with the spectrum of the bicycloaromatic hydrocarbon, trypticene. Used also by Kumler (ref. 1) for aryl ketones.

(9) W. Dieckmann and A. Kron, *Ber.*, **41**, 1269 (1908).

(10) R. P. Mariella and J. L. Leech, THIS JOURNAL, **71**, 3558 (1949).

(11) E. C. Horning, "Organic Syntheses," Coll. Vol. III, J. Wiley and Sons, Inc., New York, N. Y., 1955, p. 343.

(12) H. Rupe, A. Collin and L. Schmirderer, *Helv. Chim. Acta*, **14**, 1340 (1931).

(13) Hydrogenation of furfuralacetone gave material which contained persistent traces of starting material. The acetoacetic ester synthesis therefore was used: W. R. Kirner and G. H. Richter, THIS JOURNAL, **51**, 3131 (1929). The ketone, which reddened in air, was used only when freshly distilled.

(14) D. J. Cosgrove, D. G. H. Daniels, J. K. Whitehead and J. D. S. Gouldeo, *J. Chem. Soc.*, 4821 (1952); reddened in air; used only when freshly distilled.

(15) M. F. Carroll, *ibid.*, 1266 (1940).

(16) A. Klages, *Ber.*, **37**, 2313 (1904).

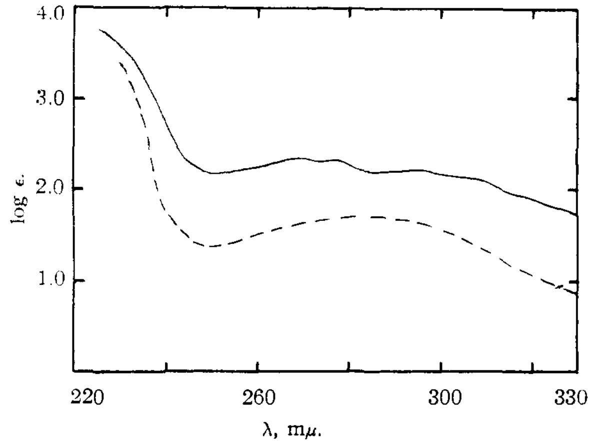


Fig. 1.—Ultraviolet absorption spectra of furfurylacetone and 2-furylacetone: ———, 2-furylacetone (C_6H_{12}); - - - -, furfurylacetone (C_6H_{12}).

Prior to application of the above values, the factor of geometry should be mentioned. In phenylacetone (III), interacted molecules have orbital axes intersecting at an angle of 70° 32′ and the orbital length necessary for intersection is 2.2 Å., based upon a C–C bond distance of 1.54 Å. For benzylacetone, the values are 141° 4′ and 1.36 Å.; for 2-phenyl-1-cycloalkanones, assuming that the ring is planar and that the phenyl group has an axis of rotation which is at an angle of 60° with the plane, 62° 30′ and 2.54 Å.; and for a rigid bicyclo molecule with single bond angles of 120° throughout, 60° and 2.66 Å. The factor of geometry thus appears to be in opposition to the factor of probability.

Since the effect of geometry cannot, as yet, be translated into quantitative terms useful in the present calculations, values of ϵ will be calculated solely from the probability factors, the discussion of geometry being reserved for criticism of results. Table I compares the spectral values for a number of cases.

Monoarylacetones are used as standards and the values for k were calculated using the simplified equation[17] $\epsilon = 20 + k/x^2$. Values for substances immediately below the standard were then calculated by equating values for k: for benzylacetone, for example, $(\epsilon_1 - 20)/x^2 = (\epsilon_2 - 20)/2x^3$, (reinterpretation).[18] In these calculations of ϵ, a value of x of 3 was used throughout. No effort is made here to refine further this value. Also, the ϵ-value of a ketone without proximity effect was assumed to be 20 throughout, in spite of well-known variations in this value (for example, Table II). Finally, for the correlation of spectral values of arylacetones with those of arylbutanones, no correction for geometry is suggested since this source of error has been absorbed by the empirical selection of the value for x; this is not true for other correlations attempted below.

Examination of Table I reveals that, *in hydrocarbon solvents, ϵ is indeed highly predictable by the equations set forth here.* This in turn suggests that Cookson's explanation of these proximity effects may be the correct one. The fact that less success is encountered with predictions in other solvents is not too disturbing in view of the great variation, with solvent, of ϵ for the principal reference substance, phenylacetone (Fig. 2).

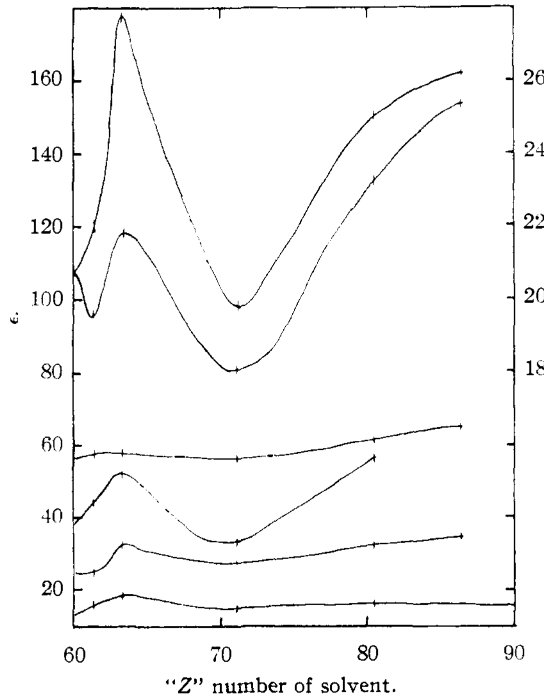


Fig. 2.—$\epsilon_{max.}$ vs. solvent "Z" number for six ketones. Ketones are, in ascending order, methoxyacetone, camphor, mesityl oxide, ethyl α-benzyl-α-propionylpropionate, 1,1-diphenylpropanone (right hand ordinate) and phenylacetone. Solvents are C_6H_{12} (60.1), EtOAc (61.5), $CHCl_3$ (63.2), MeCN (71.3), 95 wt. % EtOH (80.5) and 70 vol. % EtOH (86.4).

Results of the present work are not in accord with the hyperconjugation mechanism proposed earlier. The dimethylammonium salt group, while affecting materially the absorption of benzalacetone at short wave lengths (Fig. 3), which is the more polar absorption of the α,β-unsaturated ketone in accordance with Woodward's rule, affects hardly at all the proximity interaction in benzylacetone (Fig. 4).

An alternate explanation of the ϵ-values for ketones of the benzylacetone type should receive comment. These values, instead of being real manifestations of proximity interaction, might be merely the sum of ϵ(ketone) and ϵ(aryl "tailings"). However, four points make the latter interpretation untenable: (a) neither benzene (ϵ at 280 mμ is *ca.* 1.0)[19] nor toluene (ϵ at 280 mμ is *ca.* 1.6)[19] has "tailings" of the required magnitude; (b) nor, certainly, has furan (ϵ at 252 mμ is 1.0).[7] (c) 2-Indanone appears to be free of proximity inter-

---

[17] The more exact equation, for acetones with n aryl groups, is $\epsilon = 20(1 - 1/x^2)^n + k[1 - (1 - 1/x^2)^n]$. For cases in which $n = 1$ or 2, the error introduced by the above simplification is small.

[18] The empirical equation $\epsilon - 20 = k/(N + 5)1$ was used earlier (Abstracts of Papers, Chicago, Ill., Sept. 7-12, 1958, p. 45P) in an effort, now believed mistaken, to correlate also the spectrum of acetophenone with that of phenylacetone.

[19] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1951, Charts 7 and 8.

TABLE I

VALUES FROM THE ULTRAVIOLET ABSORPTION SPECTRA OF ARYLACETONES AND ARYLBUTANONES

	Ketone	Solvent	λ_{max}, mμ	ϵ_{max}	
				Found	Calcd.
1	Phenylacetone	C_6H_{12}	289	108	S[d]
2	Benzylacetone	C_6H_{12}	281	32[p]	35
3	1,1-Diphenyl-2-propanone	C_6H_{12}	292	210	196
4	1,3-Diphenyl-2-propanone	C_6H_{14}	294	220[a]	196
5	2-Furylacetone	C_6H_{12}	268 max.	213	S_1
			275 min.	202	
			276 max.	204	
			294 min.	149	
			297 max.	153	S_2
6	Furfurylacetone	C_6H_{12}	283	50.4	S_1 51 S_2 42
7	α-Phenylacetophenone	C_6H_{12}	330	98[b]	S
8	α-Benzylacetophenone	C_6H_{12}	330	49[b]	53
9	Phenylacetone	70% EtOH, v./v.	282	162	S
10	1,1-Diphenyl-2-propanone	70% EtOH, v./v.	285	254	304
11	*p*-Dimethylaminobenzhydrylacetone	2 *M* aq. HCl	280	46	67
12	*p*-Dimethylaminobenzylacetone	2 *M* aq. HCl	280	35	44
13	2-Furfurylacetone	95% EtOH	287	151	S
14	Furfurylacetone[c]	95% EtOH	270–273	36.5[p]	42
15	Phenylacetone	$CHCl_3$	287	178	S
16	Benzylacetone	$CHCl_3$	281	36[p]	46

[a] Data from ref. 1. [b] ε for propiophenone is 45; values are approximate and are taken from the charts of ref. 21. [c] Previously mentioned by I. Kasiwagi, *Bull. Chem. Soc. Japan*, 1, 145 (1926); *C. A.*, 21, 86 (1927). [p] Plateau. [d] Standard used to calculate values of ε below it.

action and no increase in ε(ketone) by "tailings" can be observed in its spectrum[20]; (d) slight hypsochromic shift of the benzene spectrum (by the dimethylammonium salt group (Fig. 4), which would decrease "tailings," leaves unaltered the ε-value for the ketone portion of benzylacetone. Accordingly, it is concluded that proximity interaction in benzylacetones, while small, is definite; this same view was reached previously by Kumler[1] and Ramart-Lucas.[21]

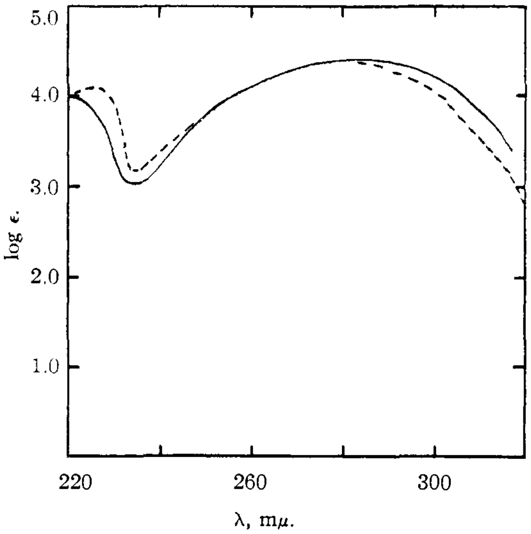


Fig. 3.—Ultraviolet absorption spectra of benzalacetone and *p*-dimethylaminobenzalacetone: ———, *p*-dimethylaminobenzalacetone (1 *M* HCl); ----, benzalacetone (heptane) (N. H. Cromwell and W. R. Watson, *J. Org. Chem.*, 14, 411 (1949)).

The ε-value for 2-phenylcyclohexanone (291 mμ, 20; EtOH)[22] does not agree with the calculated value (410, EtOH). This difference, however. is readily explicable since the aryl group is equatorially oriented[1] and the possibility of interaction is largely absent. The value for 2-phenylcyclopentanone (292 mμ, 50; EtOH)[23] suggests a similar orientation for the aryl group in this substance.[24] More significantly, perhaps, the

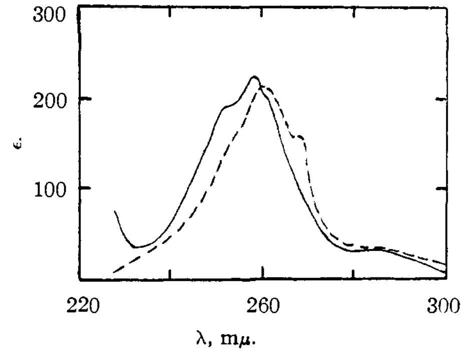


Fig. 4.—Ultraviolet absorption spectra of benzylacetone and *p*-dimethylaminobenzylacetone: ———, *p*-dimethylaminobenzylacetone (1 *M* HCl); ----, benzylacetone (alcohol).

---

(20) D. Biquard, *Bull. soc. chim.*, **8**, 55 (1941).

(21) Mme. Ramart-Lucas and M. F. Salmon-Legagneur, *ibid.*, **51**, 1069 (1932), studied many substances of formula $X-CH_2CH_2-Y$.

(22) W. C. Wildman and R. B. Wildman, *J. Org. Chem.*, **17**, 581 (1952).

(23) K. Mislow and A. K. Lazarus, THIS JOURNAL, **77**, 6383 (1955).

(24) Interpretation of the infrared spectra of halocyclopentanones has also suggested this view: F. V. Brutcher, T. Roberts, S. J. Barr and N. Pearson, *ibid.*, **78**, 1507 (1956).

TABLE II

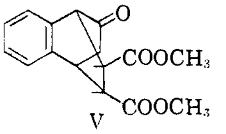
ULTRAVIOLET ABSORPTION SPECTRAL VALUES AS A FUNCTION OF SOLVENT

Ketone	λ_{max}, mμ (ϵ_{max})						
	C_6H_{12}	EtOAc	$CHCl_3$	MeCN	EtOH 95%	EtOH 70V%	H_2O
1,1-Diphenyl-2-propanone	292 (210)	292 (194)	291 (219)	290 (180)	288 (230)	285 (254)	
Phenylacetone	289 (108)	286 (121)	287 (178)	287 (97)	285 (150)[a]	282 (162)	
Ethyl α-benzyl-α-propionylpropionate	285 (56)	284 (57)	284 (57)	284 (56)	283 (61)	282 (65)	
Mesityl oxide[b]	321 (38)		315 (53)	314 (33)	310 (57)		
Camphor	293 (25)[c]	291 (25)	293 (33)	291 (28)	290 (32)[c]	287 (35)	
Cyclohexanone	292 (16)[d]	289 (15)	288 (20)	287 (16)	284 (18)		277 (20)
Methoxyacetone	282 (13)	281 (17)	279 (19)	278 (15)	276 (16)		270 (15)
Methyl isobutyl ketone	284 (22)	281 (19)	279 (21)	282 (20)	277 (23)[e]	275 (24)	

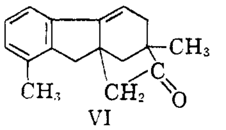
[a] In good agreement with the graph of ref. 1. [b] Data are those of E. M. Kosower (ref. 28). [c] W. G. Woods and J. D. Roberts, *J. Org. Chem.*, **22**, 1124 (1957), reported for these solvents, respectively, 292 (23) and 289.5 (32). [d] S. W. Benson and G. B. Kistiakowsky, THIS JOURNAL, **64**, 80 (1942), reported 290 (11). [e] Mme. J. Bonnier and G. de Gaudemaris, *Bull. soc. chim.*, 21, 992 (1954), reported 279 (23).

spectral value calculated for 2,2-diphenylcyclohexanone (410 EtOH) assuming that only one phenyl group is axial, also fails to agree with the actual value (298 mμ, 125; EtOH).[3] Unfortunately, however, this case is far from simple; molecular models suggest that considerable three-way interference of the two aryl groups and the cyclohexane hydrogens exists. In any case, it must be concluded that *values of ε for arylcycloalkanones are not predictable by the present calculations.*

Speculation concerning *k*, the maximum value of ϵ_{max} for substances having benzene–ketone interaction, is of interest. Values calculated from the phenylacetone data are 792 (C_6H_{12}), 1170 (EtOH) and 1422 ($CHCl_3$). The largest actual value reported by Cookson[4] (for V) is 294–295 mμ, 505 (EtOH). The calculated values, therefore, do not appear entirely unreasonable.



V



VI

The spectral value (301.5 mμ, 4,160)[25] for Gibberone (VI) suggested that β-styryl·ketone interaction could be more pronounced than phenyl·ketone interaction. The above value led to the predictions of 480 for methyl cinnamyl ketone and of 97 for cinnamylacetone. When, in the present work, cinnamylacetone was examined, it was found that the ketonic maximum was not observable (250 mμ, 19,100; 284, 1,375; 293, 930; C_6H_{12}),[26] a fact more or less anticipated since β-ethylstyrene itself has two maxima in the 280–300 mμ region (250, 15,700; 284, 1,140; 293, 750; C_6H_{12}).[27]

Since solvent effects in ultraviolet spectroscopy have been dealt with very extensively recently,[28] a few comments only concerning our data need be made. Change of solvent does not appear to alter significantly the amount of, or the number of molecules engaged in, proximity interaction. Thus, phenylacetone ε-values, which alter greatly with "*Z*" number,[28] appear much less spectacular when converted to *percentage increase of ε over cyclohexane* ε-values. These for 95% alcohol are: 1,1-diphenylpropanone-2, 9.5%; phenylacetone, 39%; ethyl α-benzyl-α-propionylpropionate, 8.9%; mesityl oxide, 50%[28]; camphor, 26%; cyclohexanone, 15%; methoxyacetone, 25%; and methyl isobutyl ketone, 4.1%. Values for chloroform are rather similar, although phenylacetone does show a somewhat greater increase (65%) than does mesityl oxide (40%).[28] In summary, only the following rather general conclusions are suggested: (1) solvent effect is superimposed upon the total ε-value, regardless of how much of this is due to proximity interaction; (2) solvent alterations of ε are due, in the main, to the steric circumstances of the oxygen of the carbonyl group and to the electronic nature of that oxygen.

KINGSTON, R. I.

---

[25] B. E. Cross, J. F. Grove, J. MacMillan and T. P. C. Mulholland, *J. Chem. Soc.*, 2520 (1958).

[26] G. R. Ames and W. Davey, *ibid.*, p. 911, gave for 3-acetonyl-5-phenyl-4-pentenoic acid 249.5 mμ, 19,500.

[27] R. H. DeWolfe, D. L. Hagmann and W. G. Young, THIS JOURNAL, **79**, 4795 (1957), reported 251 mμ, 16,300 (ether).

[28] E. M. Kosower, *ibid.*, **80**, 3253, 3261, 3267 (1958).