TABLE II

PROPERTIES OF EPOXIDES CONTAINING HYDROXYL GROUPS

Compound	B.p., °C.	Press., mm.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen % Calcd.	Hydrogen % Found	Hydroxyl No. Calcd.	Hydroxyl No. Found
Tetrahydropyran-2-methanol	57	4.2	1.4561	62.1	62.2	10.2	10.2	484	486
					62.1		10.6		487
							10.2		
3-Hydroxytetrahydrofuran	110	5.6	1.4493	54.6	54.6	9.1	9.0	638	629
					54.8		9.3		632
					54.9		9.3		
3-Ethyl-3-oxetanemethanol	84	2.8	1.4517	62.1	62.0	10.4	10.2	484	486
					62.4		10.4		483
3-Methyl-3-oxetanemethanol	80	4.0	1.4449	58.8	58.6	9.8	9.9		
					58.8		9.9	549	543
									546
3,3-Oxetanedimethanol	155	3.5	(Solid)	50.9	50.4	8.5	8.7	951	907
					50.5		8.8		906

3-Ethyl-3-oxetanemethanol from Trimethylolpropane.—A mixture of 268 g. of trimethylolpropane (2.0 moles), 236 g. of diethyl carbonate (2.0 moles) and 0.10 g. of potassium hydroxide dissolved in 5 ml. of absolute alcohol was refluxed until pot temperature was below 105° (15 minutes), and the mixture was distilled keeping the head temperature 76–78°. Distillation was continued until the pot temperature was 145°, and then the pressure was reduced gradually to 50 mm., maintaining the pot temperature at 140–150°. The weight of distillate was 179 g. (theory 184 g. alcohol). Upon heating above 180°, carbon dioxide evolution was rapid and most of the material distilled at 190–210° pot temperature, 90–140° head temperature and 50–90 mm. pressure. Near the end the pressure became 2–10 mm. and the head temperature rose. Redistillation through an efficient column gave: 13.4 g., b.p. 84–86° at 3.5 mm.; 136.6 g., b.p. 84–84.5 at 2.8 mm.; 24.4 g., b.p. 84.5-85.5 at 2.8 mm.; 26.1 g., residue.

The main fraction was analytically pure 3-ethyl-3-oxetanemethanol, and from the residue analytically pure trimethylolpropane was obtained by distillation.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Endocyclic α,β-Unsaturated Ketones. VI.[1] Ultraviolet and Infrared Absorption Spectra and Resonance Stabilizations

BY RICHARD D. CAMPBELL[2] AND NORMAN H. CROMWELL[3]

RECEIVED MARCH 1, 1957

New data are presented for the ultraviolet absorption spectra of thirteen ketones. These compounds are members of three series, *viz.*, 1,1-dimethyl-2-keto-1,2-dihydronaphthalene (1,1-dimethyl-2(1*H*)-naphthalenone) (II), 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (4,4-dimethyl-1-(4*H*)-naphthalenone) (I), and perinaphthenone-7 (1-(1*H*)-benzonaphthenone) (III). With previously reported data for eight related compounds, the spectra are discussed with respect to resonance stabilizations, effect of nature and position of substituents, and type of conjugation. New infrared spectral data are presented for twenty-one ketones in the three series. These results are discussed with respect to the same factors.

Ultraviolet Absorption Spectra Studies

Introduction.—Studies of ultraviolet absorption spectra of α,β-unsaturated ketones have mainly dealt with open chain systems, with some treatment of endocyclic series. The effect of conjugation of the unsaturated ketone system with phenyl groups has been studied, and chromophores assigned to ultraviolet absorption bands.[4,5] Absorption in the 2300–2500 Å. region was ascribed to the benzoyl or acrylophenone chromophore, and intense absorption from 2800 to 3500 Å. to the cinnamoyl chromophore. The effect of linear and crossed conjugation, and of endo- and exocyclic double bonds on the spectra of α,β-unsaturated ketones has been discussed.[6]

It was observed[4,7,8] that various substituents on the α- or β-carbon atom of the α,β-unsaturated ketone system have a bathochromic effect on the ultraviolet absorption bands. The extent of the shift varied with the nature of the substituent, and the position of attachment. Resonance forms were suggested for the chromophores responsible for the characteristic bands.[4] The importance of chelation in the β-hydroxy[7] and β-amino ketones was discussed.[4] Since such chelation or ionic interaction is impossible in the endocyclic series, it seemed of considerable interest to study these endocyclic compounds.

The compounds used in these studies are all of

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[1] For paper No. V, see, N. H. Cromwell and R. D. Campbell, *J. Org. Chem.*, **22**, in press (1957).

[2] Du Pont Teaching Fellow, 1954–1955. Ph.D. Thesis, University of Nebraska, 1956.

[3] To whom inquiries regarding this article should be addressed.

[4] N. H. Cromwell and W. R. Watson, *J. Org. Chem.*, **14**, 411 (1949).

[5] W. B. Black and R. E. Lutz, THIS JOURNAL, **77**, 5134 (1955).

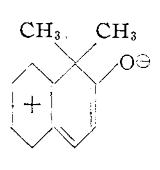
[6] H. S. French and L. Wiley, *ibid.*, **71**, 3702 (1949); H. S. French, *ibid.*, **74**, 514 (1952).

[7] K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

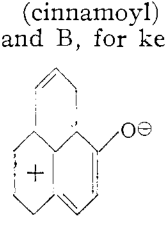
[8] A. L. Nussbaum, O. Mancera, R. Daniels, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 3263 (1951).

known structure. Their sources[9-17] are indicated in Table I. Since a detailed comparison of spectra needed to be made in order to study the effects of substituents on the spectra of the parent ketones, care was taken in imposing uniform conditions on the spectral determinations, with due regard to temperature, light exposure and solvent effects. Spectra used from the literature were checked for these conditions.

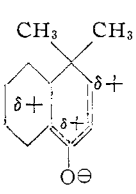
Discussion of Results.—In the three series of compounds studied, the parent endocyclic α,β-unsaturated ketones are 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (I), 1,1-dimethyl-2-keto-1,2-dihydronaphthalene (II) and perinaphthenone-7 (III). In the order named, these compounds showed strong absorption bands at successively higher intensity and longer wave length. The same result was observed in the analogous open chain compounds,[4] ethylideneacetophenone, benzalacetone and chalcone. The aromatic ring on the β-carbon atom of the α,β-unsaturated carbonyl system carries the positive charge in the longest formally polarized (cinnamoyl) structures indicated by forms A and B, for ketones II and III.



A



B



C

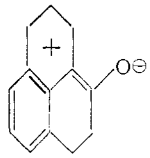
Further resonance stabilization of form B is possible. Canonical forms for III can be written with the positive charge on carbon atoms 1, 3, 4, 6, 7, 9 or 13. This accounts for the fact that the long wave length bands of III appear 500–800 Å. nearer the visible compared with the corresponding band (3000 Å.) of ketone II.

Although the extinction coefficients for the long wave length bands of II and III are nearly equal, the integrated intensity for this band of III is greater. This may be ascribed to the more extensive electronic system of III involved in the transition. Intensity of light absorption is related to the probability of the occurrence of the electronic transition, polarity of the excited state, and length of the conjugated system.[18]

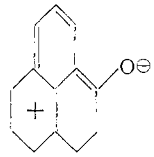
The intense absorption bands below 2500 Å. for parent ketone I and its dihydro derivative IV may be attributed to the benzoyl polarization.[4,5] The vinyl ketone system of I also is responsible for absorption in this region. Absorption in the region 2300–2400 Å. is characteristic of vinyl ketones.[6] The weak bands in the region 2800–3000 Å. for I and IV also are attributed to the benzoyl polarization.[4,5] That this band for I is more intense than for IV is the expected result because I possesses a longer conjugated system.[18] This longer conjugated system is indicated by form C above. The simultaneous interaction of the double bond and the aromatic ring with the carbonyl group cannot be described by a single valence-bond structure. It is not apparent whether such simultaneous resonance interaction is impossible or the classical structures are inadequate for these cross-conjugated systems.

The intense band (3000 Å.) due to the long conjugated system of II is wiped out in the dihydro compound V in which the conjugated system is broken. The carbonyl group in V is insulated from the benzene ring. Only a weak isolated carbonyl band[19] remains in the 2600–2900 Å. region for V. The tetralin system also absorbs weakly in this region.[20]

The extensive resonance stabilization of III is decreased in the dihydro derivative VII. This is evident from the decreased intensity and hypsochromic shift (380–450 Å.) of the absorption band in the 3000–4000 A. region. The positive charge of the polarized form of VII can be carried by either aromatic ring, as forms D and E indicate. The two forms D are expected to be more stable due to the retention of the Kekule ring. In the three forms E the Kekule structure is absent. However, the long wave length band of VII is nearer the visible and more intense than the benzoyl band of IV or the principal band of the naphthalene nucleus.[20] Hence this band of VII must involve an important contribution from forms E, as well as forms D.



D



E

Further evidence for the nature of the resonance stabilizations possible in these three series of ketones (I, II and III) is revealed in the spectra of their α-bromo derivatives VIII, XII and XV, respectively. Introduction of the α-bromo substituent onto ketone II causes a bathochromic shift of 160 Å. for the long wave length band. The α-bromo substituent was reported[8] to cause a bathochromic shift of 80–120 Å. for α,β-unsaturated ketones. The shift indicates that the bromine atom lends more resonance stabilization to the excited state than to the ground state. In addition to forms indicated by A, forms F and G might be stabilizing the excited state by supporting part of the positive charge. One may consider two or more molecular orbitals simultaneously encompassing the systems described by A, F and G.

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(9) (a) N. H. Cromwell, H. H. Eby and D. B. Capps, THIS JOURNAL, 73, 1224 (1951); (b) 72, 1230 (1951).

(10) N. H. Cromwell, D. B. Capps and S. E. Palmer, *ibid.*, **73**, 1226 (1951).

(11) R. T. Arnold, J. S. Buckley and J. Richter, *ibid.*, **69**, 2322 (1947).

(12) M. D. Soffer, *et al.*, *ibid.*, **72**, 3704 (1950).

(13) L. F. Fieser and L. W. Newton, *ibid.*, **64**, 919 (1942).

(14) L. F. Fieser and E. B. Hershberg, *ibid.*, **60**, 1658 (1938).

(15) L. F. Fieser and M. D. Gates, *ibid.*, **62**, 2335 (1940).

(16) A. M. Lukin, *Bull. Acad. Sci. U.R.S.S. Classe Sci. Chem.*, 695 (1941); *C. A.*, **37**, 2735 (1943).

(17) N. H. Cromwell and G. V. Hudson, THIS JOURNAL, **75**, 872 (1953).

(18) H. Gilman, "Organic Chemistry, an Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, Chapter 2.

(19) L. N. Ferguson, "Electronic Structures of Organic Molecules," Prentice-Hall, New York, N. Y., 1952, Chapter 9.

(20) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

TABLE I

SUMMARY OF ULTRAVIOLET AND INFRARED ABSORPTION SPECTRA OF ENDOCYCLIC α,β-UNSATURATED KETONES

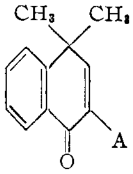
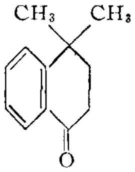
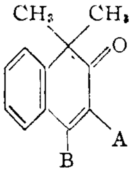
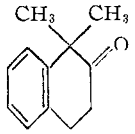
Structure	No.	Source[a]	Ultraviolet max.[b] λ(Å.)	$\Delta\lambda$[d]	$\times 10^{-3}$	Infrared C=O band[c] Wave number, cm.$^{-1}$ Nujol	CCl$_4$	$\Delta\nu$[d]
								
A = H	I	11	2300		10.7	1657	1665	..
			(2520)[e]		8.8			
			2870		2.2			
			2970		1.9			
A = Br	VIII	11	2250		5.0		1673	8
			2500	200	10.9			
			2560	260	11.0			
			(2680)		6.6			
			3010	50	1.8			
A = NC$_4$H$_8$O	IX	9b	2480	180	13.0		1662	− 3
			2890	20	2.6			
			2990	20	2.7			
			3250		1.9			
A = OCH$_3$	X	1	2200		6.6	1658	1670	5
			(2260)		5.2			
			2500	200	9.7			
			2810		6.0			
A = OH	XI	9b	2290		6.7		1649	−16
			2540	240	10.0			
			2930	60	7.7			
	IV	11	2430[i]		11.6		1685[i]	20
			2860	−10	1.4			
			2950	−20	1.1			
								
A = B = H	II	1	2300[h]		15.4	1658[g]	1662	..
			2360		15.8			
			2940		10.2			
			3000		10.1			
A = Br B = H	XII	1	2100		10.4		1678	16
			2350	50	11.7			
			2420	60	12.6			
			3160	160	13.2			
A = H B = NC$_4$H$_8$O	XIII	1	2200		9.1	1652	1670	8
			2450	90–150	15.0			
			3530	530	8.8			
A = H B = OH	XIV	1	2220		7.1	1642	1663	1
			2430	130	12.8			
			2510	150	14.5			
			3350	350	9.4			
	V	12, 1	2640[h]	−300	0.38	1710[g]	1712	50
			2720	−280	0.36			

TABLE I (*Continued*)

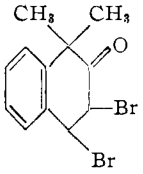
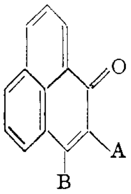
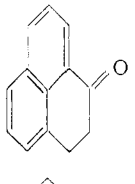
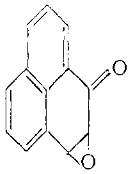
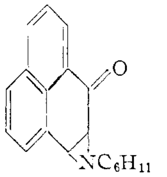
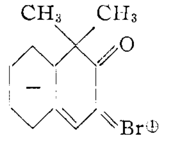
Structure	No.	Source[a]	Ultraviolet max.[b] λ(Å.)	Δλ[d]	$\epsilon \times 10^{-3}$	Infrared C=O band[c] Wave number, cm.$^{-1}$ Nujol	CCl_4	Δν[d]
	VI	1	No max.			1714	1724	62
								
A = B = H	III	14	2450^{l}		21.5	1636^{l}	1646	..
			(2600)		9.5			
			(3400)		7.5			
			3550		11.5			
			3800		9.0			
A = Br	XV	16	2100		15.0	1640	1650	4
B = H			2200		10.6			
			(2420)		15.5			
			2520		20.1			
			2600		16.1			
			3260		4.1			
			3420	20	6.2			
			3570	20	10.7			
			3810	10	8.9			
			(3920)		8.7			
A = NC_4H_8O	XVI	10	2360^{k}	− 90	21.0	1637^{k}	1640	− 6
B = H			2680		15.0			
			2740		15.3			
			3360		4.7			
			3460	− 90	5.1			
			3620	−180	5.0			
			4520		5.2			
A = H	XVII	10	2400^{k}		27.0	1633^{k}	1640	− 6
B = NC_4H_8O			3440	−110	14.0			
			3660	−140	12.0			
A = OH	XVIII	10	2370^{m}				1630	−16
B = H			(2510)					
			2590					
			(2700)					
			3160					
			3350	−200				
			3510	−290				
			4200					
A = OH	XVIII	10	2100^{f}		20.2			
B = H			2380		17.8			
			(2530)		12.8			
			2600		14.0			
			(2700)		11.6			
			3290		5.7			
			3480	(− 70)	5.4			
			3630	(−170)	6.9			
			4260		5.3			
A = H	XIX	10	2110^{f}		23.0	1626		−10
B = OH			2280		22.7			
			3330	−220	11.3			
			3520	−280	10.4			
			(3880)		4.5			

TABLE I (*Continued*)

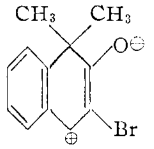
Structure	No.	Source[a]	Ultraviolet max.[b] λ(Å.)	Δλ[d]	$\epsilon \times 10^{-3}$	Infrared C=O band[c] Wave number, cm.$^{-1}$ Nujol	CCl$_4$	Δν[d]
A = NHC_6H_{11}	XX	10	2400[k]		24.0	1632[k]	1622	−24
			2700		27.4			
			3300	−250	4.6			
			3700	−100	3.0			
			5000		5.5			
	VII	15	2400[j]	− 50	19.2	1677[j]	1690	44
			2450	−100	18.5			
			3170	−380	6.5			
			3310	−450	5.5			
	XXI	13	2430[j]		9.4	1676	1683	37
			2450		9.5			
			3200	−350	8.2			
			3350	−450	8.0			
	XXII	10	2470[j]		19.0	1685[j]	1683	37
			3200	−350	7.2			
			3350	−450	6.6			

[a] Numbers are literature references which appear throughout the article. All samples were freshly purified according to the literature directions. [b] The ultraviolet–visible spectra were determined using a Cary recording spectrophotometer, Model 11 MS, according to the manufacturer's directions. The sample solutions were freshly prepared using 2,2,4-trimethylpentane (Eastman Kodak spectra grade) in suitable concentration (10^{-3} to 10^{-5} *M*). [c] The infrared spectra were determined between 700 and 4000 cm.$^{-1}$ using a Perkin–Elmer Model 21 double-beam infrared spectrophotometer. The Nujol mulls (or pure liquid) were made up to give good resolution. The determinations using carbon tetrachloride solutions were carried out in 1.0 mm. or 0.1 mm. matched cells. The concentration of these solutions was 12 mg./ml. [d] The values for Δλ and Δν were calculated by subtracting the value for the parent ketone from that of the derivative for the corresponding band, and in corresponding medium where possible. [e] Values in parentheses are shoulders. [f] Solvent was absolute methanol. [g] Pure liquid. See footnote *c*. [h] Beckman DU spectrophotometer. [i] Data from ref. 9a. [j] Data from ref. 17. [k] Data from ref. 10. [l] Data from A. Hassner, Ph.D. Thesis, University of Nebr., 1956. [m] Satd. soln.

without conflict with the Pauli exclusion principle.



F



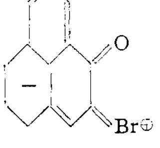
G

The bromine substituent contributes in some such indirect manner to the resonance stabilization of the excited state. It has been pointed out[8] that valence-bond structures such as A, F and G cannot be written to show the resonance contribution of the bromine atom to the polarized carbonyl system. This problem is present in any cross conjugated system.

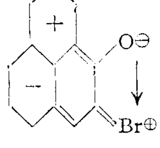
Introduction of the α-bromo substituent onto ketone I was reported[8] to give a bathochromic shift of 140 Å., using ethanol as solvent. The shift observed by us using isoöctane as solvent was 200 or 260 Å., depending on assignment of the split peak for VIII (2500, 2560 Å.). Only one peak was reported by Nussbaum, *et al.*,[8] for VIII at 2560 Å. in ethanol; the bands for I in ethanol and isoöctane are 2420 and 2300 Å., respectively. The solvent effect is as expected.[20] This solvent effect is greater with the parent ketone I than with the α-bromo derivative VIII. A generalization made by Nussbaum, *et al.*,[8] applies to these compounds: the α-bromo substituent causes a greater shift in the spectrum of phenyl vinyl ketones (*viz.*, I) than of β-styryl ketones (*viz.*, II), see Table I.

Introduction of the bromine atom onto the α-position of ketone III results in a bathochromic shift of 10–20 Å. of the long wave length bands (3300–4000 Å.). This indicates that the bromine atom hardly makes any more resonance contribution to the stability of the excited state than of the ground state. As indicated before, the positive charge of the polarized form B already is supported by extensive delocalization both in the ground state and in the excited state.

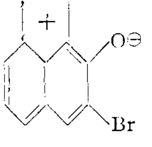
An additional triplet band (2300–2800 Å.) appears in the spectrum of XV. This triplet is characteristic of the α-substituted perinaphthenones to be mentioned later. Absorption in this region is characteristic of benzoyl polarizations stabilized by additional resonance interactions.[4,5,20] Canonical forms H, J and K, repre-



H



J



K

sent such polarizations in XV. Although the two polarized molecular orbitals implied by J cannot interact by first-order conjugation, electrostatic interaction is expected to contribute some stabilization to the polar form. One might expect that the three forms K are of very nearly the same energy, *i.e.*, degenerate states. Under the electrostatic influence of polarization H (implied in J), the degeneracy of K gives rise to the triplet (Stark effect)[21] in the 2300–2800 Å. region.

The ultraviolet spectra of the derivatives of III with N-cyclohexylamino, morpholino and hydroxyl groups in the α-position (XX, XVI and XVIII, respectively) are nearly identical.[10] These substituents result in a considerable decrease in the intensity of absorption in the 3000–4000 Å. region, and a hypsochromic shift of 90–290 Å. for these absorption maxima. This may indicate resonance interaction and stabilization in the ground state to a greater extent than in the excited state.

Two bands appear in the spectrum of the α-substituted derivatives of III, and not in the spectrum of III. One of these, in the 2300–2800 Å. region, is the triplet discussed above, and attributed to chromophores described by forms H, J and K. The triplet was not resolved in the spectrum of XX. The other new band is a broad, low intensity absorption extending into the visible region (4200–5000 Å.). This low intensity band has been reported for similar ketones.[9b,4] The shoulder (3920 Å.) in the spectrum of XV might be considered to correspond to this band characteristic of α-substituted α,β-unsaturated ketones.

The absorption maxima for the α-substituted derivatives are lower than the corresponding maxima for the parent ketone III, in the longer wave length region. However, inspection of the spectral curves shows that the integrated intensity in the region 2500–5000 Å. is greater for the α-substituted ketones. Thus the longer, intensely absorbing chromophores of the parent ketone are broken into smaller chromophores (see H, J and K) by the α-substituent. The resonance effect of the substituents is seen as an increase in the absorption over the 2500–5000 Å. range, and not in individual bands.

Introduction of the hydroxy or morpholino groups into the β-position of ketone III results in a hypsochromic shift (110–280 Å.) of the bands in the 3300–4000 Å. region. This may indicate that the substituents contribute more resonance stabilization to the ground state than to the excited state. The shift is greater for the hydroxyl group. The β-substituents introduce no bands which did not appear in III, and some fine structure is lost.[20] The increase in intensity of absorption in the 3300–4000 Å. region may be attributed to the extension of the resonating system and the greater electrical moment involved.[4,18]

The imino and epoxy derivatives have been discussed elsewhere.[10,17] The three membered ring has a small effect on the resonance in this series which is unlike the effect of either the α- or β-substituents.

Introduction of the morpholino, methoxy or hydroxy groups into the α-position of ketone I results in bathochromic shifts of 180, 200 and 240 Å., respectively, for the strong band (2300–2800 Å.), indicating resonance stabilization of the excited state with respect to the ground state.

The absorption band of I in the 2700–3100 Å. region is shifted 20–60 Å. to longer wave length (except in X) and increased in intensity by the α-substituents. The resonance stabilization of the excited state may be due to ionic forms described[4] for similar compounds. Since this is a cross-conjugated system, it is difficult to describe a polarization in which both the carbonyl oxygen and α-substituent simultaneously carry a charge, but some such interaction seems to occur.[4]

Since the electronic system of II is more closely related to benzalacetone, chalcone and ketone III than to I, the effects of substituents on the spectrum of II should follow this relationship. The β-morpholino and β-hydroxy groups cause bathochromic shifts (530 and 350 Å., respectively) of the cinnamoyl band of II. This is consistent with the effect observed in other series.[4,7,22,23] That the effect of the amino group is greater is consistent with its greater electromeric effect.[19] In those cases in which hydrogen bonding is possible[4,22,23] the effect of hydroxyl is greater. Intramolecular hydrogen bonding is not possible in XIV. One might predict that the unknown α-hydroxy derivative of II would have a cinnamoyl band shifted about 300 Å. to longer wave length from the corresponding band of II, and with little more than one-half of the intensity.[4,23] One might also expect a broad, low intensity band extending into the visible region.[9b,4]

The spectral studies in the three series, I, II and III result in the following conclusions:

1. The effects of substituents on α,β-unsaturated ketones vary widely not only with the nature of the substituent, but also with the position of the substituent in the molecule and the steric and electronic nature of the ketone system.
2. In the perinaphthenone-7 (III) system, extensive resonance interaction is indicated both in the ground state and excited state.
3. In the cross-conjugated system (I), the substituent effects are small.
4. In the linear conjugated system (II), the substituent effects are larger.

Infrared Absorption Spectra Studies

Introduction.—The infrared absorption by ketones due to the carbonyl stretching vibration has been intensively studied. Factors influencing the polarity of the carbonyl group, and thus the absorption frequency, have been discussed.[24] Most of the studies of such factors have dealt with the immediate environment of the carbonyl group, with some study of the farther-reaching resonance effects. Conjugation effects of aryl and olefinic groups in open chain compounds have been

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[21] H. S. Taylor and S. Glasstone, "A Treatise on Physical Chemistry," Vol. I, 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 281.

[22] B. Eistert, F. Weygand and E. Csendes, *Ber.*, **84**, 763 (1951).

[23] T. M. Lowry, H. Moureu and C. A. H. MacConkey, *J. Chem. Soc.*, 3171 (1928).

[24] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 9.

studied.[24,25] Some substituent effects have been investigated,[25,26] but not with endocyclic α,β-unsaturated ketones. Hydrogen bonding effects have been observed.[24,27] Such effects might operate in α-substituted endocyclic α,β-unsaturated ketones but would be geometrically impossible in the β-derivatives.[4]

For some of the compounds involved in this study, infrared data have been determined using Nujol mulls. It has been pointed out[24,25] that intermolecular forces in condensed phases have an important influence on the infrared carbonyl absorption frequency. These forces can be minimized by using dilute solutions in carbon tetrachloride.

The discussion above, concerning the ultraviolet spectra of these compounds, dealt with some evidence for the effect of the various substituents on the ground state of the endocyclic α,β-unsaturated carbonyl system. It seemed of interest to obtain the more direct evidence of infrared spectra for these effects, and to study these spectra in relation to each other and to previous infrared data.[24]

Discussion of Results.—The physical state of the sample is important.[24] In dilute carbon tetrachloride solution the carbonyl band generally was found to be 10–20 cm.$^{-1}$ toward higher wave numbers than the carbonyl band observed in the condensed phase (*viz.*, liquid or Nujol mull). In some cases the difference was less, particularly in the perinaphthenone-7 (III) series. In the condensed phase, intermolecular effects might be expected to increase the polarity of the carbonyl group. Thus the solution data give a more reliable picture of the isolated molecule.[25] In the discussion which follows, references will be made almost exclusively to the solution data.

The carbonyl absorption frequency gives evidence of the polarity (single bond character) of the carbonyl group. The normal undisturbed carbonyl frequency is 1705–1725 cm.$^{-1}$ in aliphatic ketones.[24] Conjugation with an aryl group reduces the wave number to 1680–1700 cm.$^{-1}$. Phenyl vinyl ketones and β-styryl ketones absorb in the same range[25] (*viz.*, 1680 and 1690 cm.$^{-1}$, resp.).

Endocyclic ketones I and II absorb at 1665 and 1662 cm.$^{-1}$, respectively. This indicates that resonance interaction causes the carbonyl groups to be slightly more polar than in the corresponding open chain compounds.[25] The cyclic conjugated systems in I and II are held rigidly in position for maximum resonance interaction and polarization.[28] Perinaphthenone-7 (III) shows even more extensive resonance interaction between the carbonyl group and the rest of the aromatic system. The carbonyl absorption frequency (1646 cm.$^{-1}$) indicates considerable polarity of the carbonyl group. Evidence for this extensive resonance interaction in the ground state of III and its derivatives was also noted in the ultraviolet spectra.

The dihydro derivatives in the three series exhibit carbonyl bands in the range expected. Ketone V has an aliphatic carbonyl group, and absorbs at 1712 cm.$^{-1}$. Ketones IV and VII are aryl ketones, and absorb at 1685 and 1690 cm.$^{-1}$, respectively. The α-bromine atom in VI shifts the absorption band 12 cm.$^{-1}$ to higher wave number, as expected.[24]

In all three series of unsaturated ketones, introduction of a bromine atom into the α-position caused a shift to higher wave numbers. This indicates that the strong inductive and coulombic field effects of bromine increase the double bond character of the carbonyl group. Several workers[24] have observed that the shift caused by an equatorial α-bromine was 20 cm.$^{-1}$ in saturated ketones, where only the inductive and coulombic field effects can operate. In the II, I and III series, the shift is progressively less (16, 8, and 4 cm.$^{-1}$, respectively). This indicates that the resonance and electrostatic dipolar interaction[29] of the bromine atom with the carbonyl group is progressively greater for the three series in the order named, and partly cancels the inductive and coulombic field effects, see Fig. 1. The resonance stabilization of the excited state for these compounds has been discussed above, in relation to the ultraviolet spectra.

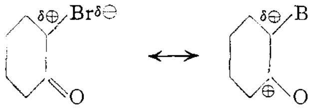

Fig. 1.—Coulombic field effect: equatorial bromine tends to suppress this indicated resonance in saturated cyclic ketones; see R. N. Jones, *et al.*, THIS JOURNAL, **74**, 2830 (1952).

The effect of the β-morpholino or β-hydroxyl group on the carbonyl band of open chain α,β-unsaturated ketones is varied. Where hydrogen bonding (resonance chelation)[24] is possible, the β-amino group[27] reduced the carbonyl band wave number 50–60 cm.$^{-1}$. Even in the absence of

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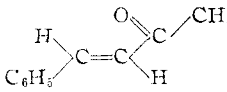
[25] N. Fuson, M. L. Josien and E. M. Shelton, THIS JOURNAL, **76**, 2528 (1954).

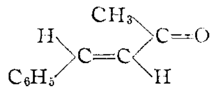
[26] A. H. Soloway and S. L. Friess, *ibid.*, **73**, 5000 (1951).

[27] N. H. Cromwell, *et al.*, *ibid.*, **71**, 3337 (1949).

[28] In this Laboratory Prof. H. E. Baumgarten has recently measured the infrared spectrum of highly purified benzalacetone. Using Nujol mulls, bands were found at, 1688(V.S.); 1665(W); 1615–1605 (V.S.); 1585(S); 6 mg./ml. CCl$_4$ in 1.0 mm. matched cells, 1699 (79% abs.); 1678 (94% abs.); 1617 (92% abs.). We believe that a C=O band assignment should be made to both the 1688–1699 and 1665–1678 cm.$^{-1}$ bands. The strong 1617–1605 cm.$^{-1}$ bands are probably composite C=C and conjugated phenyl bands. The two C=O bands are apparently associated with two possible rotational isomers of *trans*-benzalacetone; see footnote *b*, Table I, N. H. Cromwell and R. J. Mohrbacher, THIS JOURNAL, **75**, 6254 (1953).



S-*cis*-*trans* (labile)
(C=O$_{CCl_4}$ band, 1699 cm.$^{-1}$)



S-*trans*-*trans* (labile)
(C=O$_{CCl_4}$ band, 1678 cm.$^{-1}$)

The endocyclic ketone II might be expected to have its C=O band (1662 cm.$^{-1}$) nearer to that of the S-*trans*-*trans* form of benzalacetone than to that of the S-*cis*-*trans* comformation. Fuson, *et al.*, ref. 25, have reported C=O bands at 1700–1685 cm.$^{-1}$ and C=C bands at 1670–1662 cm.$^{-1}$ for various β-styryl ketones. We suggest that these lower frequency bands might best be assigned to the carbonyl group of the S *trans*-*trans* forms of these compounds; see E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3771 (1955). House, THIS JOURNAL, **78**, 4394 (1956); **79**, 1490 (1957), reported C=O bands for 2-benzalcyclohexanone-1 (an S-*cis*-*trans* structure) and 3-phenyl-2-cyclohexenone-1 (an S-*trans*-*trans* structure) at 1685 and 1660 cm.$^{-1}$, respectively.

[29] See form J above. The indicated (→) electrostatic interaction should aid resonance.

chelation, the shift is approximately 30 cm.$^{-1}$ to lower wave number.[27] In the endocyclic compounds the chelation and dipolar[10] interaction effects are expected to be absent. In series II, the β-morpholino group effect seems anomalous, *i.e.*, it causes a shift of 8 cm.$^{-1}$ to higher wave number. It has been observed[27] that the resonance effect of the β-amino group is less in β-styryl ketones than in phenyl vinyl ketones. It would seem that in XIII the resonance effect of the morpholino group is less than its electron-withdrawing inductive effect.[30] The inductive effect of an α-bromine atom causes a shift in the same direction (see above). The β-hydroxyl group of XIV causes a shift of 1 cm.$^{-1}$ to higher wave length; again the expected[24] shift is to lower wave length. Here resonance and inductive factors are nearly balanced.

In the perinaphthenone-7 (III) series, the β-morpholino and β-hydroxyl groups cause shifts of the carbonyl band of 6 and 10 cm.$^{-1}$ to lower wave number. The shifts indicate that the carbonyl group has developed more single bond character through resonance interaction with the substituents, but the effect is smaller than in open chain compounds.[27] In XVII and XIX, intramolecular hydrogen bonding and dipolar[10] effects are not possible Also, the parent ketone system of III is extensively resonance stabilized, so the resonance effect of the substituents is less important.

Introduction of substituents into the α-position of parent ketone III results in shifts of the carbonyl band to lower wave numbers, indicating a more polar carbonyl group. The shifts for the α-morpholino, α-hydroxy and α-cyclohexylamino groups are -6, -16 and -24 cm.$^{-1}$, respectively. In the latter two (*viz.*, XVIII and XX), a five-atom chelate ring is possible. Intramolecular hydrogen bonding seems to increase the polarity of the carbonyl group in these compounds. The problem of direct resonance interaction between the carbonyl group and α-substituents has been discussed (see ultraviolet spectra discussion).

In series I, the effects of α-substitution on the polarity of the carbonyl group vary according to the nature of the substituent. It has been noted above and elsewhere,[24,27] that the inductive (electron withdrawing) effect of α-substituents decreases the polarity of the carbonyl group (shift to higher wave number), whereas the resonance effect and intramolecular hydrogen bonding give the opposite result. On the basis of electronegativity, and inductive effects,[31] the expected order of decreasing electron withdrawing (inductive) effect for the substituents is: bromo, hydroxy, methoxy and morpholino. The shifts caused by the α-substituents are: bromo, 8 cm.$^{-1}$; methoxy, 5 cm.$^{-1}$; morpholino, -3 cm.$^{-1}$; and hydroxy, -16 cm.$^{-1}$. For the bromo and methoxy substituents, the inductive effect is more important than the resonance effect. In the morpholino derivative IX the resonance effect is more important. Here the resonance effect may be aided in some manner by dipole interaction.[4] The hydroxyl group in XI seems to engage in intramolecular hydrogen bonding, thus increasing the polarity of the carbonyl group. In XI the resonance and hydrogen bonding effects of the substituent are considerably more important than the inductive effect on the polarity of the carbonyl group.

For the epoxy and imino derivatives of III, (XXI and XXII, respectively), the infrared spectra of Nujol mulls were reported[10,17] and discussed[17] in terms of the steric requirements of the three-ring for resonance interaction. It was suggested by N. Fuson[25] that data obtained in carbon tetrachloride solution would be necessary, to isolate the effect of the three-ring on the carbonyl frequency. Now these data are reported, and the previous conclusions[17] are essentially confirmed.

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation, N.S.F., G-1091.

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[30] Resonance interaction of the morpholino group with the unsaturated ketone system may be somewhat inhibited sterically in this structure.

[31] C. K. Ingold "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 67.