two kinds of methyl proton coupling constants is estimated as of the order of microseconds or longer. The absence of any change in the spectrum over a 120° temperature range is evidence for a large energy barrier to rotation about the carbon–nitrogen bond. We suggest that the differing nonbonded interactions between methyl groups and the remainder of the radical are responsible for observation of different spin densities in the α- and β-positions. It should be noted that related phenomena have been observed in the e.s.r. spectra of a number of anion radicals.[23-26]

Wiberg and Buchler[2] found that the p.m.r. spectrum of TDE^{+2} showed two absorptions of equal intensity which differed in chemical shift by 0.28 p.p.m. They attributed the observation to the absence of free rotation about the $C-N(CH_3)_2$ bond and pointed to a similar observation for dimethylformamide.[27]

The ratio, R, of methyl proton coupling constant to nitrogen coupling constant has values of 0.68 and 0.59 in TDE^{+}. These values are anomalously low by comparison with R-values for related radicals such as Wurster's blue, 0.97, and $(CH_3)_3N^{+}$, 1.48. Such low values may arise from enhancement of the nitrogen coupling constant or it is possible that structural perturbations described in the preceding section may be responsible for depression of the methyl proton coupling constant. Whichever the case, there is not now an unequivocal basis for establishing which of the coupling constants should be attributed to the β-methyl protons. We do wish to suggest that the smaller coupling constant of 2.84 G. probably should be identified with the β-methyl protons. This conclusion is based on the näive argument that the β-methyl protons are subject to a larger nonbonded electronic interaction which in turn is properly correlated with the larger deviation of the R-value of 0.59 from the values of 0.97 and 1.48 as cited above.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

Keto–Enol Tautomerism in β-Dicarbonyls Studied by Nuclear Magnetic Resonance Spectroscopy.[1] I. Proton Chemical Shifts and Equilibrium Constants of Pure Compounds

BY JANE L. BURDETT AND MAX T. ROGERS

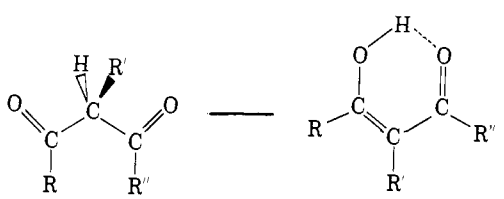
RECEIVED DECEMBER 14, 1963

The tautomeric equilibria of β-dicarbonyls have been investigated by nuclear magnetic resonance (n.m.r.) spectroscopy. Proton chemical shift measurements have been made for a series of acyclic compounds, and equilibrium constants ([enol]/[keto]) have been determined. Substituent effects on proton chemical shifts and on equilibrium constants have been noted.

Keto–enol tautomerism has been studied for many years by techniques such as bromine titration and infrared and ultraviolet spectroscopy. Nuclear magnetic resonance spectroscopy, like other spectroscopic methods, provides the opportunity of investigating the tautomeric equilibrium without affecting the position of the equilibrium itself.

Jarrett, *et al.*,[2] examined the n.m.r. spectra of acetylacetone and α-methylacetylacetone and showed that the spectra of the tautomers could be distinguished; however, they could not resolve the acetyl methyl or α-methyl protons of the tautomers. Reeves[3a] studied acetylacetone and Giessner-Prettre[3b] ethyl acetoacetate by the n.m.r. method. Forsen and Nilsson[4] have made an extensive investigation of enolized β-triketones using both n.m.r. and infrared spectroscopy.

The present study has involved a series of β-dicarbonyls, both β-diketones and β-keto esters, principally of the acyclic variety. The keto–enol tautomeric equilibrium which is considered in this study is shown below where (a) is the keto tautomer and (b) is the enol tautomer. Separate resonance signals are nearly al-



(a) keto (b) enol

ways observed for the protons of the various groups in the keto and enol tautomers. Identification of these peaks has been possible from the chemical shifts and spin–spin splittings combined with integration of the relative intensities of keto and enol resonances for a given compound. In some cases solvent effects or variable temperature studies have been used to confirm the assignments. For example, dilution in hexane which increases the percentage enol tautomer made it

(1) This work was supported through a contract with the Atomic Energy Commission and a grant from the National Science Foundation, and is abstracted in part from the Ph.D. thesis of Jane L. Burdett, Michigan State University, 1963.
(2) H. S. Jarrett, M. S. Sadler, and J. N. Shoolery, *J. Chem. Phys.*, **21**, 2092 (1953).
(3) (a) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957); (b) C. Giessner-Prettre, *Compt. rend.*, **250**, 2547 (1960).
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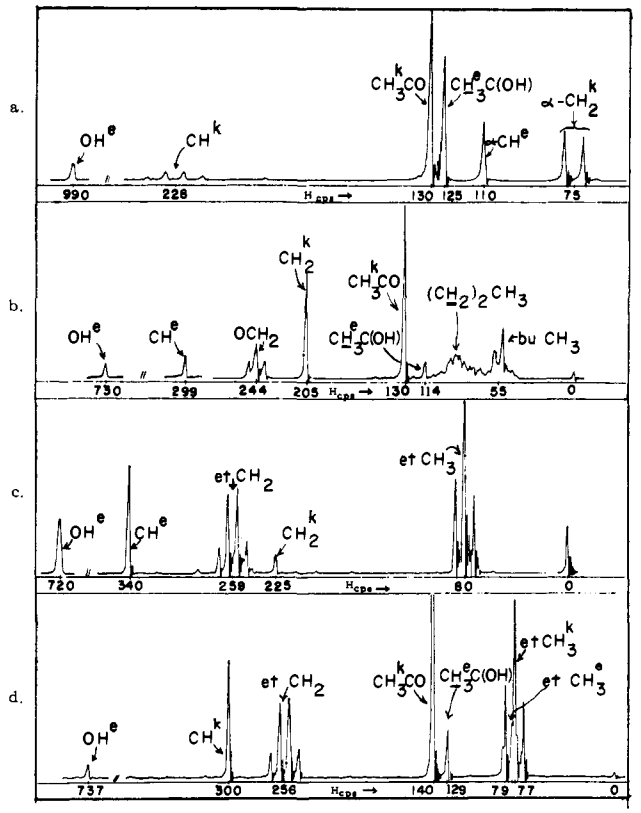

Fig. 1.—Proton n.m.r. spectra of: a, α-methylacetylacetone; b, butyl acetoacetate; c, ethyl trifluoroacetoacetate; d, ethyl α-chloroacetoacetate.

possible to confirm the enol resonance peaks in ethyl α-methylacetoacetate. The keto protons of trifluoroacetylacetone have been assigned by using high temperatures which favor the keto tautomer.

Experimental

Instrumental.—Proton magnetic resonance spectra were obtained on the Varian A-60 spectrometer. Chemical shift and equilibrium constant measurements have been made at 33–35°. Chemical shift values are reported in c.p.s. from internal tetramethylsilane to within ±1 c.p.s. Equilibrium constants have been obtained by integration of keto and enol resonance peaks. At least six integrations have been performed, and the percentages of enol tautomer are accurate to within ±2%.

α-Chloroacetylacetone was synthesized according to the method of D'Amico.[5] Fractional distillation at 14 mm. and 41.0–44.5° gave the product ($n^{20.3}$D 1.4749).

α-Bromoacetylacetone was synthesized according to the method of Schwarzenbach and Felder[6] after preparing the copper complex of acetylacetone according to the method of Ciocca.[7] The product as a yellow liquid was fractionally distilled at 13 mm. and 60°.

***n*-Butyl α-chloroacetoacetate and *t*-butyl α-chloroacetoacetate** were prepared by modifications of the procedure of D'Amico.[5] Sulfuryl chloride (34 g.) was added dropwise to *n*-butyl acetoacetate (40 g.) with stirring at 0° over a 2-hr. period. The mixture was neutralized with 10% aqueous sodium bicarbonate (150 ml.) and extracted with ether (150 ml.) in three portions. The extract was dried, the ether removed by distillation, and the product vacuum distilled at 5 mm. and 84–86° as a pale yellow liquid ($n^{20.3}$D 1.4463). *t*-Butyl acetoacetate was treated in the same manner as *n*-butyl acetoacetate. The ether extract was washed with water to neutralize it and then dried. The ether was removed by distillation, and the product was vacuum distilled at 3 mm. and 59–61° as a pale yellow liquid ($n^{20.3}$D 1.4450).

β-Bromoethyl acetoacetate was synthesized according to Donaruma[8] from β-bromoethanol and ethyl acetoacetate by ester exchange, using PbO as a catalyst. Fractional distillation at 7 mm. and 112–114° gave the product ($n^{20.3}$D 1.4750).

Ethyl γ-bromoacetoacetate was prepared by the method of Burger and Ullyot.[9] The product was distilled at 84–85° and 5 mm. as a pink liquid.

Ethyl α-Cyanoacetoacetate.—Isoshima's preparation in which ketene is treated with ethyl α-cyanoacetate was used to make ethyl α-cyanoacetoacetate.[10] The ethyl α-cyanoacetate along with an equimolar amount of pyridine, was heated to 80° before introduction of ketene, and ketene was fed in for a period of 3.5 hr. The reaction mixture was shaken occasionally. The solution was neutralized, and the pyridine removed by distillation. The compound was fractionally distilled at 88–89° at 6 mm. as a colorless liquid ($n^{20.3}$D 1.4710).

Ethyl α-bromoacetoacetate was prepared according to the procedure of Kharasch, *et al.*,[11] by the action of bromine on the parent ester. The product was distilled at 94–94.5° and 11 mm. as a colorless liquid ($n^{20.3}$D 1.4622).

Other Materials.—Butyl acetoacetate and ethyl α-isopropylacetoacetate were synthesized for us by Eastman Organic Chemicals, Distillation Products Industries. The remaining compounds were commercial samples purified by the usual recrystallization, fractional distillation, and vapor phase chromatographic techniques. Purity was checked by melting point, boiling point or refractive index measurement, and by gas chromatography. Refractive indices were obtained on the Bausch and Lomb, Type 33-45-56 refractometer. Vapor phase chromatography was performed on the Perkin-Elmer Model 154A (20% silica column) and Aerograph Model A-700 (30% silica column).

Results and Discussion

Chemical Shifts of Pure β-Dicarbonyls.—Proton chemical shifts are given in Table I for β-diketones and in Table II for β-keto esters in c.p.s. from internal tetramethylsilane. Representative n.m.r. spectra of the β-dicarbonyls are shown in Fig. 1.[12] In general the resonance position for the acetyl methyl protons and the alkoxy protons does not vary appreciably among the compounds studied. The keto α-protons are deshielded by the substitution of electron-withdrawing groups in the α-position. Both keto and enol α-protons are deshielded by substitution of electron-withdrawing groups in place of the acetyl methyl group.

The enol OH protons show considerable variation in chemical shift, particularly among the β-diketones, but all are at very low applied magnetic fields indicating the presence of intramolecular hydrogen bonds in these compounds. Forsen and Nilsson[4] have shown that a linear relationship exists between the chelated carbonyl stretching frequency and the chemical shift of the enol OH. Their results are plotted in Fig. 2, and line B represents the linear relationship for the β-triketones suggested by them. A lower carbonyl stretching frequency corresponds to a lower chemical shift of the enol OH and presumably a stronger intramolecular hydrogen bond. Results from the present study are plotted in Fig. 2, and line A represents the best straight line through these points. Values of the chelate carbonyl stretching frequencies have been taken from the literature; where several values are available, the average was used. Frequencies of the carbonyl group have been obtained in the present work for ethyl trifluoroacetoacetate, hexafluoroacetylacetone, and trifluoroacetylacetone from infrared spectra. The β-dicarbonyls studied here do not follow the strict

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(12) Spectra for all the β-dicarbonyls listed in Tables I and II may be found in the Ph.D. thesis of J. L. Burdett, Michigan State University, 1963.

TABLE I

PROTON CHEMICAL SHIFTS IN PURE β-DIKETONES[a,b]

Compound	Acetyl		α-Proton				Other
	CH_3^e	CH_3^k	CH_2^k	CH^k	CH^e	OH^e	
Acetylacetone	120	130	217	...	334	934	...
α-Chloroacetylacetone	133	137	...	292	...	922	...
α-Bromoacetylacetone	138	143	...	301	...	951	...
Cyclic isopropylidene malonate (in CCl_4)	...	...	107	...	...	..	105 $(CH_3)_2$
Dibenzoylmethane (in CCl_4)	...	...	...	...	382	1020	422 6 ring H's
							455 4 ring H's
Hexafluoroacetylacetone	...	...	248	...	386	780	...
Trifluoroacetylacetone	132	136	237	...	360	847	...
1,3-Indanedione (in dioxane)	...	...	191	...	...	..	...
α-Methylacetylacetone	125	130	...	228	...	990	75^k α-CH_3
							110^e α-CH_3
1-Phenyl-1,3-butanedione (0.401 *M* in CCl_4)	120	127	231	...	357	980	...
2-Phenyl-1,3-indanedione	...	...	...	270	...	..	...
Thenoyltrifluoroacetone (0.301 *M* in CS_2)	...	...	...	...	382	898	...

[a] Chemical shifts are in c.p.s. from TMS. [b] ^{k} = keto; ^{e} = enol.

TABLE II

PROTON CHEMICAL SHIFTS IN PURE β-KETO ESTERS[a,b]

Compound	Ethyl		Acetyl		α-Proton				Other
	CH_3	CH_2	CH_3^e	CH_3^k	CH_2^k	CH^k	CH^k	OH^e	
β-Bromoethyl acetoacetate	..	269	119	126	215	...	307	712	218 $EtCH_2Br$
Butyl acetoacetate	..	...	114	130	205	...	299	730	244 $BuOCH_2$
									55 $BuCH_3$
t-Butyl acetoacetate	..	...	112	130	199	...	293	733	86 $(CH_3)_3$
n-Butyl α-chloroacetoacetate	..	...	129	140	...	298	...	740	254 $BuOCH_2$
									55 $BuCH_3$
t-Butyl α-chloroacetoacetate	..	...	128	139	...	287	...	747	89 *t*-Butyl^e
									92 *t*-Butyl^k
Ethyl acetoacetate	74	249	117	133	209	...	302	730	...
Ethyl α-allylacetoacetate	73	248	117	129	...	214	...	770	151 $CH_2CH{=}CH_2$
									303 $CH{=}CH_2$
									347 $CH{=}CH_2$
Ethyl α-isoamylacetoacetate	73	248	m	128	...	202	...	762	52 $(CH_3)_2$
Ethyl benzoylacetate	67^k	246^k	...	...	238	...	342	770	...
	73^e	253^e							
Ethyl α-bromoacetoacetate	77^k	257	134	144	...	303	...	764	...
	79^e								
Ethyl γ-bromoacetoacetate	76	253	...	...	226	...	325	716	258 $BrCH_2CO$
Ethyl α-isobutylacetoacetate	73	248	m	128	...	210	...	773	53 $CH(CH_3)_2$
Ethyl α-*n*-butylacetoacetate	73	249	m	128	...	205	...	771	53 $BuCH_3$
Ethyl α-chloroacetoacetate	77^k	256	129	140	...	300	...	737	...
	79^e								
Ethyl α-cyanoacetoacetate	83	263	142	...	...	...	...	807	...
Ethyl α-ethylacetoacetate	74	250	m	130	...	204	...	764	53 $EtCH_3$
Ethyl α-fluoroacetoacetate	78^k	258^k	...	138	...	327	...	...	
	73^e	212^e							
Ethyl trifluoroacetoacetate	76^k	255^k	...	...	225	...	340	720	...
	80^e	259^e							
Ethyl α-methylacetoacetate	74	248	119	130	...	212	...	758	75 α-CH_3
Ethyl α-isopropylacetoacetate	73	249	132	129	...	194	...	779	54^k $CH(CH_3)_2$
									301^e $CH(CH_3)_2$
Ethyl α-*n*-propylacetoacetate	73	249	m	128	...	207	...	768	56 $PrCH_2$
Methyl acetoacetate	..	...	...	125	280	...	...	...	125 OCH_3

[a] Chemical shifts are in c.p.s. from TMS. [b] ^{k} = keto; ^{e} = enol; m = masked.

linear relationship found for β-triketones by Forsen and Nilsson, particularly for those β-dicarbonyls containing halogen atoms.

Tautomeric Equilibria of Pure β-Dicarbonyls.—For most β-keto esters the equilibrium is on the side of the keto tautomer (see Fig. 1b). The percentages of enol tautomer and the corresponding equilibrium constants are given in Table III for each β-diketone, and in Table IV for each β-keto ester studied. The keto tautomer (a) is pictured with the carbonyls opposed in the configuration which is electrostatically most favorable. In the esters there is little steric interaction between R and R″ because the OR″ group increases the mean R–R″ distance.

For β-diketones, however, the nonbonded van der Waals interactions between R and R″ become important. The tautomeric equilibria for the β-diketones then favor the enol tautomers (see Table III). The enol tautomer (b) exists as the intramolecularly hydrogen-bonded species in all the compounds studied (with the possible exception of ethyl α-fluoroacetoacetate). Wheland estimated that the intramolecular hydrogen

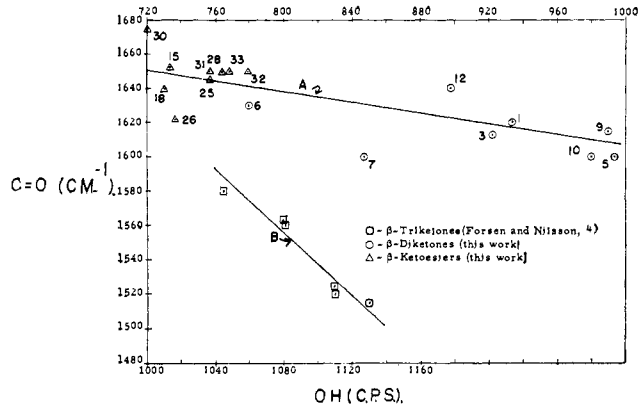

Fig. 2.—Chemical shift of enol OH proton *vs.* carbonyl stretching frequency for β-dicarbonyls. (Code numbers refer to compounds of Tables III and IV.)

bond of acetylacetone stabilizes the enol tautomer by 5–10 kcal., and the conjugated system further stabilizes this tautomer by 2–3 kcal.[13]

TABLE III

PERCENTAGES OF ENOL TAUTOMERS AND EQUILIBRIUM CONSTANTS FOR β-DIKETONES AS DETERMINED BY NUCLEAR MAGNETIC RESONANCE

Code	Compound	Enol, %	K_e[a]	Proton signals integrated
1	Acetylacetone	81	4.3	CH^e/CH_2^k
2	α-Bromoacetylacetone	46	0.85	CH_3^e/CH_3^k
3	α-Chloroacetylacetone	94	16	CH_3^e/CH_3^k
4	Cyclic isopropylidene malonate (in CCl_4)	0	0	...
5	Dibenzoylmethane (in CCl_4)	100	...	...
6	Hexafluoroacetylacetone	100	...	...
7	Trifluoroacetylacetone	97	32	CH_3^e/CH_3^k
8	1,3-Indanedione (in $CHCl_3$)	0	0	...
9	α-Methylacetylacetone	30	0.43	$\alpha\text{-}CH_3^e/\alpha\text{-}CH_3^k$
10	1-Phenyl-1,3-butanedione (in CCl_4)	100	...	...
11	2-Phenyl-1,3-indanedione (in dioxane)	0	0	...
12	Thenoyltrifluoroacetone (in CS_2)	100	...	...

[a] K_e = [enol]/[keto], and all measurements are at 33 ± 2°.

In both β-keto esters and β-diketones the substitution of bulky α-substituents results in steric hindrance between the R′ and R (or R″) group protons, particularly in the enol tautomer. The effect of alkyl substitution in the α-position is seen by the large reduction in the percentage enol for such compounds. This is presumably a combination of the steric effects mentioned and of inductive effects. The electron density in the vicinity of the α-protons should be increased by the substitution of alkyl groups at the α-position.

For both β-diketones and β-keto esters, substitution of an electron-withdrawing group such as chlorine in the α-position results in an increase of enol tautomer. However, bromine causes a marked decrease in enolization. This is presumably largely the result of the greater van der Waals nonbonded interactions between bromine and the acetyl methyl protons than between chlorine and the acetyl protons, but bromine is also less electronegative than chlorine. The highly electronegative perfluoromethyl groups in trifluoroacetylacetone, hexafluoroacetylacetone, and ethyl trifluoroacetoacetate lead to a large percentage of enol tautomer in these compounds. Although Park, *et al.*,[14] have suggested stabilization of the *cis* tautomer in trifluoroacetylacetone by an α-H · · · F intramolecular bond, molecular models show that such a bond would involve a strained five-membered ring and a CHF angle less than 90°. Substitution of a cyano group in the α-position of ethyl acetoacetate results in a shift to over 90% enol tautomer. A molecular model indicates that the possibility of –CN · · · α-H bonding in the enol tautomer is not a likely one. It would appear that the high enol content in both cases is a result of electron withdrawal from the region of the α-proton. Also, in the enol tautomer the electronegative group in the α-position is further from the carbonyl group and electrostatic repulsions should be less.

In dibenzoylmethane, 1-phenyl-1,3-butanedione, and thenoyltrifluoroacetone the presence of the aromatic ring results in an increase in enolization. In no case is the aromatic ring able to assume a position parallel to the intramolecular six-membered ring of the enol tautomer because of steric interaction with the enol α-proton, and the conjugated system is therefore not extended. Stabilization of the enol tautomer must then result from an electron-withdrawing effect of the ring. Neither 1,3-indanedione nor 2-phenyl-1,3-indanedione gives evidence of enolization in solvents such as chloroform, benzene, dioxane, or dichloroethane. This is not surprising since molecular models indicate that the formation of an intramolecularly-bonded system is precluded by steric considerations. Likewise, cyclic isopropylidene malonate cannot form an intramolecular hydrogen bond and is completely ketonic in carbon disulfide, carbon tetrachloride, benzene, and chloroform.

The substitution of an alkyl group larger than ethyl on the alkoxy end of the acetoacetate molecule results

TABLE IV

PERCENTAGE ENOL TAUTOMERS AND EQUILIBRIUM CONSTANTS FOR β-KETO ESTERS AS DETERMINED BY NUCLEAR MAGNETIC RESONANCE

Code	Compound	Enol, %	K_e[a]	Proton signals integrated
13	β-Bromoethyl acetoacetate	6	0.06	CH_3^e/CH_3^k
14	Butyl acetoacetate	15	.18	CH^k/ethyl CH_2
15	*t*-Butyl acetoacetate	17	.21	$(CH_3)_3^e/(CH_3)_3^k$
16	Butyl α-chloroacetoacetate	20	.25	CH^k/OH^e
17	*t*-Butyl α-chloroacetoacetate	46	.85	CH_3^e/CH_3^k
18	Ethyl acetoacetate	8	.09	CH_3^e/CH_3^k
19	Ethyl α-allylacetoacetate	~3	~ .03	Peak heights
20	Ethyl α-isoamylacetoacetate	~3	~ .03	Peak heights
21	Ethyl benzoylacetate	22	.28	$CH^e/(CH_3)_3^{e+k}$
22	Ethyl α-bromoacetoacetate	5	.05	Peak heights
24	Ethyl α-isobutylacetoacetate	~2	~ .02	Peak heights
25	Ethyl α-*n*-butylacetoacetate	~2	~ .02	Peak heights
26	Ethyl α-chloroacetoacetate	15	.18	CH^k/ethyl CH_2
27	Ethyl α-cyanoacetoacetate	93	13	OH^e/CH_2^{e+k}
28	Ethyl α-ethylacetoacetate	~1	~0.01	Peak heights
29	Ethyl α-fluoroacetoacetate	15	0.18	CH^k/ethyl CH_2
30	Ethyl trifluoroacetoacetate	89	8.1	CH^e/CH_3^k
31	Ethyl α-methylacetoacetate	5	0.05	CH^k/ethyl CH_2
32	Ethyl α-isopropylacetoacetate	~1	~ .01	Peak heights
33	Ethyl α-*n*-propylacetoacetate	~1	~ .01	Peak heights
34	Methyl acetoacetate	0	0	...

[a] K_e = [enol]/[keto], and all measurements are at 33 ± 2°.

(13) G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960.

(14) J. D. Park, H. A. Brown, and J. R. Lacher, *J. Am. Chem. Soc.*, **75**, 4753 (1953).

in increased enolization. This may be explained by steric interaction between the alkoxy protons and those of the acetyl methyl group in the keto tautomer. This interaction forces the carbonyls into a position in which the electrostatic repulsion between carbonyls is larger and consequently results in a shift in the position of equilibrium toward the enol tautomer.

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General Characteristics of Magneto-optical Rotation Spectra

BY VICTOR E. SHASHOUA

RECEIVED NOVEMBER 27, 1963

The magneto-optical rotation (m.o.r.) spectra of a number of optically inactive substances were obtained through a study of magnetically induced optical rotations (Faraday effect) as a function of wave length in the ultraviolet and visible regions of the spectrum. Several different types of characteristic spectra were observed at the absorption regions of molecules, and these have been tentatively classified into five spectral types. The instrumentation and technique of measurement using magnetic field strengths of 10,000 gauss are described. Typical m.o.r. spectra of organic molecules, such as acetone, phenazine, acridine, furan, and inorganic molecules, such as cobaltous salts, potassium ferricyanide, nickel sulfate, etc., are illustrated. The results, to date, indicate that m.o.r. spectroscopy might extend the scope of the optical rotatory dispersion method to a wide variety of optically inactive molecules.

Introduction

One of the most useful methods developed in recent years for the study of the stereochemistry of simple and macromolecules is the optical rotatory dispersion (o.r.d.) technique.[1] In this method, the optical rotation of plane polarized light is studied as a function of wave length to give an o.r.d. spectrum. The method, however, is limited to naturally optically active molecules and cannot be applied to the vast majority of compounds which are optically inactive.

In a previous communication from these laboratories[2] magneto-optical rotation (m.o.r.) spectroscopy was described as a possible means of extending the optical rotatory dispersion method to all molecules, irrespective of whether they possess natural activity; m.o.r. spectroscopy is based on Faraday's[3] discovery, in 1846, that any molecule will rotate the plane of polarized light when a magnetic field is applied parallel to the light beam. Verdet[4] studied the Faraday effect and showed that, at a fixed wave length, the optical rotation θ was related to the magnetic field strength H, and the path length of the sample L, by the equation

$$\theta = VHL$$

where V is a constant known as the Verdet constant.

In a review of the literature on the Faraday effect, Partington[5] points out that aside from sporadic attempts to measure the rotation at different wave lengths, most of the work of the past 120 years was confined to measurements at the sodium D-line wave length. Perkin,[5] in numerous papers, correlated stereochemical features of molecules with magnetic rotations measured at the sodium D-line wave length. Becquerel[6] described some of the first dispersion measurements. Cotton and Scherer[7] were the first to carry out dispersion measurements on cobaltous chloride in the absorption region of the molecules. These results have been confirmed in more recent investigations.[8,9]

In addition, magneto-optical rotation studies in the vicinity of the absorption bands are discussed by Roberts and Stone for cerous sulfate[10] and titanium tetrachloride.[11] Garner, Nutt, and Labbauf[12] described a study of various hydrocarbons. More recently, Eberhardt[13] investigated the magnetic rotation spectra of certain diatomic molecules and gaseous organic molecules, such as formaldehyde. It is of interest to note that the Faraday effect is quite a general phenomenon and has been observed in the microwave region,[14] infrared region,[15] X-ray region,[16] as well as in the visible and ultraviolet regions of the electromagnetic spectrum. The literature, however, contains no systematic studies of optical rotations as a function of wave length in the absorption regions of molecules.

This paper describes the results of an experimental investigation of m.o.r. spectroscopy, in the ultraviolet and visible regions of the spectrum, to determine the general characteristics of m.o.r. spectra in the absorption regions of molecules. Through a rigorous study of the experimental problems in measurement, a number of instrumental errors was found in our initial results.[2] These difficulties were eliminated in a new apparatus specially constructed for this work. The major objective of this study was to determine whether magneto-optical rotation spectra exhibit anomalous dispersion features at the absorption band regions of molecules and, if so, to correlate spectral features with molecular structure.

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