[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

The Ultraviolet Absorption Spectra of Enolizable β-Ketonitriles[1]

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The positions of the keto–enol equilibrium of several ketonitriles in a variety of solvents have been determined spectrophotometrically. The results lend support to the views on the effect of solvent on the tautomeric equilibrium which have been expressed previously.[2]

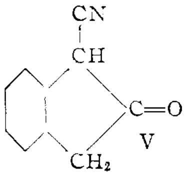
In an earlier communication[2] it was demonstrated spectrophotometrically that the β-ketonitrile cyanodesoxybenzoin (I) and some closely related compounds were enolized to a greater extent in polar than in non-polar solvents. Since the enolic form of cyanodesoxybenzoin (Ib), and in fact of all β-ketonitriles, is incapable of chelation, the low enolization in non-polar solvents was attributed to the low solubility of this (hydroxylic) form in these solvents in accordance with the van't Hoff–Dimroth equation: $K = G(S_E/S_K)$ (where G is a constant independent of the solvent and S_E and S_K are the solubilities of the enolic and ketonic forms respectively in this solvent). Since the publication of these results Eistert and Reiss[3] have also demonstrated that cyclic β-dicarbonyl compounds, giving rise to non-chelated enols, are more enolized in polar than in non-polar solvents.

It seemed of interest to study the absorption spectra of a number of β-ketonitriles of widely different structures in a variety of solvents. For this purpose α-propionyl-*p*-chlorophenylacetonitrile (II),[4] α-(N,N-dimethylaminoacetyl)-*p*-chlorophenylacetonitrile (III),[4] ω-cyanoacetophenone (IV)[5] and 1-cyanohydrindan-2-one (V)[6] were selected.

$$\underset{\text{Ia}}{\text{Ph—CH(CN)—COPh}} \rightleftarrows \underset{\text{Ib}}{\text{Ph—C(CN)=C(OH)Ph}}$$

$$\underset{\text{II}}{\text{ClC}_6\text{H}_4\text{CH(CN)COCH}_2\text{CH}_3} \qquad \underset{\text{IV}}{\text{PhCOCH}_2\text{CN}}$$

$$\underset{\text{III}}{\text{ClC}_6\text{H}_4\text{CH(CN)COCH}_2\text{N(CH}_3)_2}$$



V

The spectrum of II in ethanol shows an intense peak at 274 mμ (*E* 17,300) (Table II) with a step out at about 325 mμ (*E ca.* 2,300). When the spectrum is measured in acidified ethanol (*ca.* 0.01 *N*) the main peak falls at the same wave length but with a slightly higher intensity (*E* 18,700). The slight step out at 325 mμ is not now visible. Comparison of the spectrum of II in neutral or acidified ethanol with that of the corresponding enol ether VI[7] in alcohol reveals that the intense band at 274 mμ occurs in the spectrum of the enol ether also, and with approximately the same intensity. This leads to the conclusion that in ethanol α-propionyl-*p*-chlorophenylacetonitrile (II) is completely enolized. The intensity of the "enol peak" at 274 mμ

$$\underset{\text{VI}}{\text{ClC}_6\text{H}_4\text{C(CN)=C(OC}_2\text{H}_5)\text{CH}_2\text{CH}_3}$$

therefore may be used as a measure of the enol content of solutions of II. In hydroxylic solvents the intensity of this peak in acidified solution (0.01 *N* hydrogen chloride) is the better criterion since in neutral hydroxylic solution the ketonitrile, a rather strong acid (*pK* 6.3), dissociates to some extent giving observable absorption at about 310 mμ. While this effect is slight in ethanol, it becomes considerable in water.

In non-polar solvents the intensity of the "enol peak" is quite low. The main peak now falls at 226 mμ (*E* 11,700) in cyclohexane. This is the type of spectrum which might be anticipated for the ketonic form of II since this form contains no chromophore capable of intense absorption above 230 mμ. The spectrum in chloroform shows the low "enol peak"; however, the 226 mμ peak is not apparent since the solvent is not transparent in this region. The spectrum in ether is intermediate between that in alcohol and that in cyclohexane. The enol contents of solutions in various solvents are given in Table I.

TABLE I

ENOL CONTENTS OF SOLUTIONS OF α-PROPIONYL-*p*-CHLOROPHENYLACETONITRILE IN VARIOUS SOLVENTS (CONC. 10 MG./LITER)

Solvent	$E_{274\ \text{m}\mu}$[a]	Enol, %
Water[b]	6,300	33
Methanol[b]	16,000	84
Ethanol[b]	18,700	98
Ether	12,000	60
Chloroform	1,500	7.5
Cyclohexane	1,000	5

[a] α-*p*-Chlorophenyl-β-ethoxy-β-ethylacrylonitrile ("pure enol" reference), $E_{274\ \text{m}\mu}$ 19,000, in alcohol or cyclohexane. [b] Solution approx. 0.01 *N* HCl.

Figures for the enol content of this ketonitrile, determined by other methods, are not available. However, Arndt and co-workers[8] have determined the enol content of solutions of α-acetylphenylacetonitrile in ethanol and methanol to be 91 and 85.8%, respectively. Infrared measurements indicate that II exists in the enolic form in the crystalline state.[9]

The values in Table I show clearly the two trends noticed in the study of cyanodesoxybenzoin and its relatives.[2] These are: the decrease in enol content

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(1) Paper read before the Organic Section of the American Chemical Society, Cincinnati, Ohio, April 1, 1955.

(2) P. B. Russell, THIS JOURNAL, **74**, 2654 (1952).

(3) B. Eistert and W. Reiss, *Ber.*, **87**, 92, 108 (1954).

(4) P. B. Russell and G. H. Hitchings, THIS JOURNAL, **73**, 3763 (1951).

(5) S. Gabriel and E. Eschenbach, *Ber.*, **30**, 1127 (1897).

(6) C. W. Moore and J. F. Thorpe, *J. Chem. Soc.*, **93**, 165 (1908).

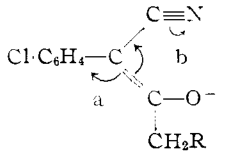
(7) P. B. Russell and N. Whittaker, THIS JOURNAL, **74**, 1310 (1952).

(8) F. Arndt, L. Löwe and R. Ginkök, *Istanbul Univ. Fen Fac. Mecmuasi*, **A11**, 154 (1946).

(9) B. H. Chase and J. Walker, *J. Chem. Soc.*, 3518 (1953).

with increasing solvating power of the solvent and the decrease in enol content on passing from a polar to a non-polar solvent. The first trend is regarded[2,3] as being due to the solvation of the keto form forcing the tautomeric equilibrium in this direction. The second, as has been mentioned, is considered to be due to the low solubility of the hydroxylic (non-chelated) enol in non-polar solvents.

The spectrum of the ketonitrile in alkaline solution at *p*H 13, that is, the spectrum of the mesomeric anion VII, shows two clear bands: at 250 mμ (*E* 9,000) and 310 mμ (*E* 17,000). It is considered that the longer wave length band corresponds to the main enol chromophore, absorbing at 274 mμ, moved to the longer wave lengths by conversion to the anionic state as is usual. This chromophore corresponds to the canonical structures VIIa, involving the aromatic ring. The second band at 250 mμ is considered to be due to a competing chromophore VIIb, which does not involve the aromatic group. In confirmation of this view it was found that cyanoacetone in alkaline solution at *p*H 13 shows a single sharp peak at 252 mμ (*E* 12,000). The undissociated enol corresponding to the mesomeric ion VIIb would be the so-called "enimide-form." It is unlikely that this isomer is included in the tautomeric equilibrium mixture. The presence of such tautomers has been demonstrated by Arndt and co-workers,[10] using diazomethane, in equilibrium solutions of such substances as methyl α-*p*-toluenesulfonylcyanoacetate and α-*p*-toluenesulfonylmalononitrile. Cyanoketones, however, tautomerized exclusively toward the keto group to form a true "enol."[11]



VII, R = $—CH_3$

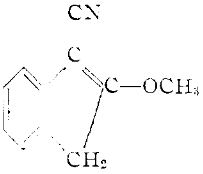
VIII, R = $—\dot{N}H(CH_3)_2$

The condensation of ethyl N,N-dimethylaminoacetate and *p*-chlorophenylacetonitrile in the presence of sodium ethoxide gives a compound $C_{12}H_{13}ON_2Cl$.[4] It was expected that this compound would have the structure III and that in its properties it might resemble II. However, the properties of the compound differed considerably from those that had been anticipated. Notably it was much less soluble in organic solvents and melted some 100° higher than did II. Further, it did not give an O-methyl compound with diazomethane, and with ferric chloride in methanol or ethanol it gave an intense blue color. With the former reagent, compounds of type II give O-methyl derivatives rapidly and in good yield[4] while with the latter they give transient greens becoming blue only on addition of a little carbonate. In view of such unusual properties the zwitterionic structure VIII was suggested for the compounds $C_{12}H_{13}ON_2Cl$.[4]

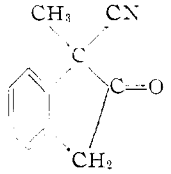
An examination of the ultraviolet spectrum of this compound, $C_{12}H_{13}ON_2Cl$,[4] confirms the structure VIII. In absolute alcohol the spectrum is almost indistinguishable from that of the ion VII; in acidified alcoholic solutions, on the other hand, the absorption maxima fall at 273 mμ (*E* 15,500). This indicates that the cationic enol is the main form present.

It is apparent from the ultraviolet spectrum and other properties that α-anilinoacetyl-*p*-chlorophenylacetonitrile has a zwitterionic structure similar to VIII. α-(N-Phenyl-N-methylaminoacetyl)-phenylacetonitrile on the other hand gives only a weak blue with ferric chloride, gives an O-methyl ether with diazomethane and melts in the region anticipated by comparison with II. The absorption spectrum of this compound in neutral alcohol shows only one intense band at 260–270 mμ although absorption in 270–330 mμ region is generally higher than is usual with compounds of type II. It would appear that α-(N-phenyl-N-methylaminoacetyl)-phenylacetonitrile is mainly in the non-zwitterionic form, corresponding to III and its enol. The departure from the zwitterionic structure must be a result of a decrease in base strength due to the bulky substituents.

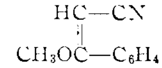
The spectrum of 1-cyanohydrindan-2-one (V) is essentially the same in all organic solvents. It consists of two bands at 226 mμ (*E* 15,500) and 274 mμ (*E* 8,500), with a step out at about 310 mμ (2,500). This spectrum is almost indistinguishable from that of the corresponding methyl ether, 1-cyano-2-methoxyhydrindene (IX),[6] but differs from that of the ketone, 1-cyano-1-methylhydrindan-2-one (X),[6] a model for the keto form, which shows no selective absorption above 230 mμ.[12] This indicates that V is completely enolized under all conditions. In water the spectrum is somewhat different, showing peaks at 220 mμ (*E* 13,000), 260 mμ (*E* 10,500) and 285 mμ (*E* 12,000). This spectrum is intermediate between that in alcohol and that in alkaline solution (at *p*H 13 max. at 220 mμ (*E* 16,500), 265 mμ (*E* 15,000) and 295 mμ (*E* 17,000)). It is apparent that 1-cyanohydrindan-2-one is extensively ionized in aqueous solution and is therefore a strong acid. Titration confirms this view; the *pK* of the compound is 4.8.



IX



X



$$\begin{array}{c} HC—CN \\ \| \\ CH_3OC—C_6H_4 \end{array}$$

XI

The spectrum of ω-cyanoacetophenone (IV) in ethanol shows two peaks. The first, the more intense, falls at 245 mμ (*E* 13,000) and is due to the keto form.[2] The second, the "enol peak," is little more than a step out at 275–280 mμ (*E* 2,000). The *trans*-enol ether, *trans*-β-methoxy-β-phenylacrylo-

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(10) F. Arndt, H. Scholz and E. Frobel, *Ann.*, **521**, 95 (1935).

(11) F. Arndt, 28th Annual Priestly Lectures, 1954, Pennsylvania State University, p. 30.

(12) The compound (X) was prepared by the method of Moore and Thorpe.[6] The oil, which had the characteristics described by these authors, showed a low peak at 265–275 mμ (*E* 2,500). The methylation was carried out with methyl iodide in methanolic potassium hydroxide and it was thought that this low peak was due to about 20–30% of the O-methylation product. This is not unlikely since with ethyl iodide under the same conditions the O-ethyl compound is the main product. Chromatography of the crude methylation product (1.5 g.) in hexane–benzene on alumina gave in the first band about 0.3–0.4 g. of the methyl ether IX. Unfortunately the ketone X could not be recovered unchanged.

nitrile (XI)[13] shows only one peak at 273 mμ (E 15,000). The enol content of an ethanol solution determined from the above figures is 13.5%; in water the enol content is about 10% while in cyclohexane the value is 6.0%. Arndt and co-workers[8] found that in ethanolic solution at a concentration of $^1/_{400}$ M the ketonitrile IV was some 12% enolized. The agreement between the present values of enol content and those determined by the Meyer method is quite satisfactory. The limited number of determinations carried out on ω-cyanoacetophenone shows that change of solvent affects the enol contents in the same general way as with α-propionyl-p-chlorophenylacetonitrile and cyanodesoxybenzoin and its relatives.[2]

The spectrum of ω-cyanoacetophenone in alkaline solution, unlike that of II and of V under the same conditions, has only a single peak at 308 mμ (E 9,300). There is no maximum about 250 mμ. It is apparent that in the anion of this compound the cyanoketone chromophore cannot operate independently of the benzene ring. ω-Cyanoacetophenone is a weak acid (pK 8.0); the spectrum in water shows no evidence of dissociation.

It is apparent from what has been said above that the spectrophotometric method gives values of the enol concentrations for the ketonitriles examined which are in good agreement with those determined by the Meyer method. It must be remembered that this method utilizes solutions which are much more dilute than the $^1/_{200}$ or $^1/_{400}$ M solutions used in the classical method. Further, the spectrophotometric method utilizes the enol ether as a "pure enol" reference and this might be expected to introduce some error. However, despite the errors in the absolute magnitude of the enol contents, the effects of various solvents are clearly defined.

Experimental

Compounds.—The compounds were prepared by the methods of the authors cited. Before spectroscopic examination they were crystallized several times from the appropriate solvent; liquids were distilled at least twice.

Ultraviolet absorption spectra were determined in solution in the various solvents at a concentration of 10 mg./l. The spectra of the tautomeric substances were determined after equilibrium was attained, usually in a few minutes. A Beckman model DU quartz spectrophotometer (cell length 1 cm.) was used. The results are given in Table II.

***pK* Values** were determined by titration of 1 millimole of the crystalline acid dissolved in 10 ml. of 50% aqueous methanol with 0.1 N sodium hydroxide, the pH of the solution being determined continuously.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF KETONITRILES AND RELATED COMPOUNDS (CONCN. 10 MG./L.)

		Spectrum	
Compound	Solvent	$\lambda_{\min}$, mμ ($E \times 10^{-3}$)	$\lambda_{\max}$, mμ ($E \times 10^{-3}$)
			226(11.7)
II	Cyclohexane	246(0.8)	274(1.0)
II	Chloroform		274(1.5)
II	Ether	240(4.8)	274(12.0)
II	Ethanol	235(5.0)	274(17.3)
			320–330(2.2) Stp-t.
II	Ethanol (0.01 N HCl)	235(5.0)	274(18.7)
II	Methanol (0.01 N HCl)	235(5.0)	274(16.0)
II	Water–methanol (90:10)	240(3.8)	260(5.0) Infl.
			280(6.2) Max.
II	Water–methanol (90:10; 0.01 N HCl)	240(3.8)	274(6.0)
II	Water (0.01 N NaOH)	235(6.0)	250(9.0)
		270(7.7)	310(17.0)
VI	Alcohol	235(5.7)	274(19.0)
III	Ethanol (0.01 N HCl)	235(5.0)	273(15.5)
III	Ethanol	235(6.0)	250(8.5)
		270(7.7)	310(16.4)
IV	Ethanol	220(2.5)	245(13.0)
		270(1.9)	275–280(2.0)
IV	Cyclohexane	*ca.* 220	245(12.5)
		269(0.7)	280(0.9)
XI	Alc. or cyclohexane	232(6.5)	272(15.0)
IV	0.01 N NaOH	260(3.0)	308(9.3)
			225(15.5)
V	Ethanol (0.01 N HCl)	252(4.2)	274(8.5)
			305–310 Infl. (2.4)
			225(12.0)
V	Cyclohexane	250(3.0)	270(7.0)
			275–280 (Infl. 5.8)
			300–305(Stp-t. 1.1)
IX	Alc. or cyclohexane	250(3.5)	272(9.5)
			275–280(8.2 Infl.)
			300–305(3.9 Infl.)
V	Water		220(13.0)
		235(7.0)	260(10.5)
		273(9.5)	285(12.0)
V	0.01 N NaOH		220(16.5)
		235(5.7)	265(15.6)
		273(11.6)	295(17.0)

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(13) F. Arndt and L. Loewe, *Ber.*, **71**, 1631 (1938).