

ide until precipitation was complete. The salts were filtered off and recrystallized from ethyl acetate. Yields were quantitative. The potassium salts decompose explosively at, or near, their melting points which are as follows: potassium I, 170–171°; potassium II, 205–206°; potassium III, 191–192°; potassium IV, 174–175°. Due to the explosive nature of these salts they were not subjected to elemental analysis. Ultraviolet spectra of the salts were identical with those of the free alkyl nitraminotetrazoles in water or in an equivalent amount of dilute potassium hydroxide solution.

2-Aminopyridine salts of alkyl nitraminotetrazoles were prepared by treating an ethereal solution of the appropriate alkyl nitraminotetrazole with an equivalent amount of 2-aminopyridine dissolved in ether and recrystallizing from 1:1 isopropyl alcohol-ethyl alcohol. Yields were quantitative. Melting points and analyses are given in Table III.

Potentiometric titrations were done using a Beckman Model G pH meter. Approximately 0.01 molar solutions of the alkyl nitraminotetrazoles in water were titrated with standard 0.1*N* aqueous potassium hydroxide at $25 \pm 0.02^\circ$. The results are summarized in Table I.

Ultraviolet absorption spectra were determined with a Beckman model DU spectrophotometer with approximately 1×10^{-4} molar aqueous solutions of the alkyl nitraminotetrazoles or their potassium salts. Spectra of the alkyl nitraminotetrazoles in an equivalent amount of aqueous potassium hydroxide and of 5-nitraminotetrazole with two equivalents of aqueous potassium hydroxide were also determined. The location of maxima and minima and extinction coefficients is given in Table IV.

EAST LANSING, MICH.

[CONTRIBUTION FROM THE COURTAULD INSTITUTE OF BIOCHEMISTRY]

Vibrational Frequencies of Isatin Oximes

D. G. O'SULLIVAN AND P. W. SADLER

Received August 22, 1956

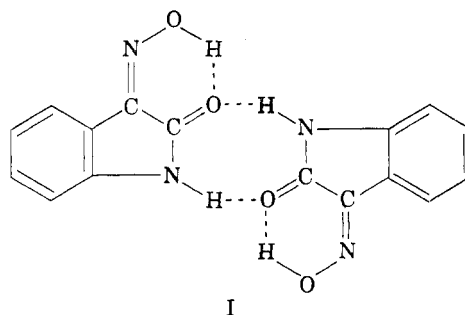
The infrared spectra of a set of substituted isatin- β -oximes and related compounds indicate that the former contain both intra- and intermolecular hydrogen bonding. Comparatively large shifts in the α -carbonyl group stretching frequencies occur with variation in ring substituents similar to the shifts observed with substituted oxindoles and with substituted acetanilides in the solid state. These shifts increase with the appropriate σ values of the substituents. Frequencies associated with the oxime group occur near 1660, 1200, and 1000 cm^{-1} and are referred to C=N stretching, N—O—H deformation and N—OH stretching modes, respectively. The 1660 cm^{-1} band is of variable intensity. The medium intensity deformation mode decreases in frequency with increase in the σ value of the substituent, while the 1000 cm^{-1} band is the strongest in the spectrum and increases in frequency with the σ value. Lower frequency ring vibrations are correlated with the substitution pattern.

Few systematic data are available on the infrared spectra of oximes. Palm and Werbin¹ found that α - and β -oximes in nujol mulls possessed associated OH stretching frequencies near 3250 and 3150 cm^{-1} , respectively, and bands near 1650, 1300, and 920 cm^{-1} which were ascribed to C=N stretching, OH deformation and N—OH stretching vibrations. Duyckwerts² provided further data in a study of some oximes and their metal coordination complexes. Substituted isatin- β -oximes were examined for information on their structure, on the position of bands characteristic of the oxime group and for the effect of substituents on these frequencies. A number of possible isomeric structures exist for these compounds, together with a considerable variety of hydrogen-bonded association complexes. Infrared results obtained with isatin- β -oximes substituted in the benzene ring are consistent with the assumption that formula I represents the structure and mode of association of compounds of this type. Other association forms appear less likely.

Free OH and NH stretching absorptions, to be expected near 3650 and 3450 cm^{-1} , respectively,

(1) A. Palm and H. Werbin, *Can. J. Chem.*, **31**, 1004 (1953).

(2) G. Duyckwerts, *Bull. soc. roy. sci. Liège*, **21**, 196 (1952).



are absent from all oximes in Table I. Intense absorption near 1720 cm^{-1} , produced by the stretching vibrations of the carbonyl group, and the presence, in some cases, of a C=N stretching frequency near 1660 cm^{-1} confirm the usually ascribed molecular structures, but the existence of an intense and broad band between 3200 and 2600 cm^{-1} indicates that the structures are involved in extensive hydrogen bonding. N-Methylindoxyl oxime II, which can associate only through the oxime groups, possesses a broad band of medium intensity with a fairly sharp maximum at 3210 cm^{-1} in accordance with the behavior of simpler oximes.¹ The sharp and lower intensity band at 2922 cm^{-1} in both N-methylindoxyl oxime and isatin is produced by CH stretching vibration. Remaining compounds in Table I possess an intense broad band near 3200

cm.⁻¹ and a broad band of slightly lower intensity near 2900 cm.⁻¹ The former occurs in the region characteristic of the CO...H—N linkage as illustrated in Table I by isatin. This and the absence of a free NH frequency near 3450 cm.⁻¹ in the oximes agree with the suggestion that the 3200 cm.⁻¹ band is, at least in part, produced by an amide type of association. The presence of a similar, but somewhat less intense, band in N-methylisatin oxime, in which amide association is absent, indicates that the 3200 cm.⁻¹ band does not arise entirely from this cause. The absorption near 2900 cm.⁻¹ is too intense and broad to be attributed solely to the CH frequency and must also be referred to association involving the oxime group. An OH stretching absorption at this low wave number implies that hydrogen bonding in these compounds is stronger than is usually the case in simpler oximes. This strengthening can be achieved by resonance involving III and IV producing an intramolecularly-bonded hybrid. Structure III must be the main contributor as all the compounds possess strong carbonyl absorptions, but the latter are displaced to lower frequencies than that of isatin, confirming the increase in single bond character of this group. Further confirmation arises from the appearance of a single very broad weak band between 3200 and 2600 cm.⁻¹ in both N-methylisatin oxime and 5-methylisatin oxime when the compounds were examined in chloroform solution. Intramolecular hydrogen bonding should not be markedly affected under these conditions.

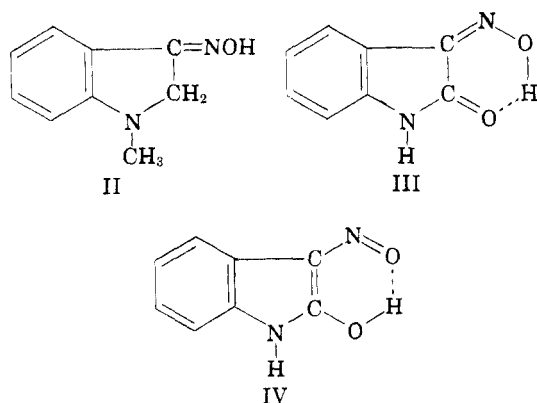


Table I shows that, if the 5-methoxy compound is excluded, the carbonyl frequency increases with the σ value³ of the substituent taken with reference to the NH group, indicating that the normal effect of the substituents is transmitted to the carbonyl group *via* the NH group as in substituted acetanilides⁴ and oxindoles.⁵

The C=N stretching frequency near 1650 cm.⁻¹

(3) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940, p. 188.

(4) D. G. O'Sullivan and P. W. Sadler, *J. Org. Chem.* (in the press).

(5) A. E. Kellie, D. G. O'Sullivan, and P. W. Sadler, *J. Chem. Soc.* (in the press).

TABLE I

HAMMETT'S σ VALUES WITH REFERENCE TO THE Ar-NH LINKAGE AND CO FREQUENCIES OF ISATIN- β -OXIMES

Substituent	M.P., °C.	σ	Frequency ^a
5-MeO	248	-0.268	1734
5-Me	248	-0.170	1710
6-Me	230	-0.069	1712
None	224	0	1712
5-F	282	0.062	1712
6-F	240	0.337	1720
6-I	195	0.352	1725
6-Cl	255	0.373	1727
6-Br	244	0.391	1727
7-Br	263	—	1733
7-NO ₂	>300	—	1731
1-Me	194	—	1703
Compound			
Isatin	203	—	1730

^a All peaks are of high intensity.

is variable. Occasionally it is split into two very weak peaks and frequently it is absent. Intense absorption on either side of this region may obscure the absorption produced by the C=N group in some cases. No correlation exists between this frequency and the σ constants of substituents with respect to this position. A number of maxima occur near 1300 cm.⁻¹ but no characteristic absorption referable to the oxime group appears to exist in this neighborhood. Many types of vibration such as Ar—N, Ar—C, and other ring frequencies and CO deformation modes may be responsible for these peaks which are listed, together with the benzene ring frequencies near 1620, 1480, and 1450 cm.⁻¹, in Table II. A number of frequencies related to substituents also occur in this region, such as the strong asymmetric and symmetric NO₂ stretching absorptions at 1526 and 1350 cm.⁻¹ in 7-nitroisatin oxime. However, at about 1200 cm.⁻¹ strong or medium absorption occurs in all the isatin oximes, which is much more intense than that feature of ortho disubstituted benzenes, the weak maximum at 1208 cm.⁻¹ which is present in isatin. As shown in Table III the frequencies tend to decrease with increase in the σ values of the substituents in virtue of their position in relation to the Ar—C linkage. This absorption is provisionally referred to the N—O—H bending vibration. All the oximes show absorption in the 1020 cm.⁻¹ region which is usually the most intense absorption in the spectrum. This band is completely absent in the parent ketones and is undoubtedly characteristic of the oxime group in this series. These frequencies appear to increase with the σ constants of the substituents as shown in Table III. They are probably produced by the N—OH stretching mode, as the C—OH stretching frequency in alcohols is responsible for a strong band in the 1200 to 1000 cm.⁻¹ region. The strong band near 980 cm.⁻¹ reported by Palm and Werbin¹ is likely to be shifted to higher frequencies in isatin oximes, one contributing cause being the

TABLE II
 FREQUENCIES IN THE 1630 TO 1250 CM.⁻¹ REGION

Substituent							
None	1621 s			1467 s	1393 w	1350 s	1301 w
1-Me	1617 s		1498 w	1460 m	1385 m	1348 m	1318 vw
5-MeO	1607 m		1489 s	1444 w	1400 vw	1320 m	1303 m
5-Me	1630 m		1482 m	1446 w	1403 vw	1324 m	
5-F	1621 s		1478 s	1458 s	1408 w	1330 m	
6-Me	1630 s			1450 m		1355 m	1300 vw
6-Br	1616 s		1478 m	1440 s		1362 m	1341 m
6-I	1615 s		1478 m	1437 m		1360 m	1342 m
7-Br	1621 s		1480 w	1437 s			1342 s
7-NO ₂	1626 s	1526 s	1474 s	1445 w	1398 vw	1350 m	1334 s
Compound							
Isatin	1620 s			1469 m	1405 w		1338 m
II ^a	1616 m		1481 m	1433 w	1382 vw		1343 m

^a N-methylindoxyl oxime.

 TABLE III
 FREQUENCIES BELOW 2000 CM.⁻¹ ASSOCIATED WITH THE OXIME GROUP

Substituent	σ	Frequencies					
6-Me	-0.170			1240 m	1200 m		1025 s
5-Me	-0.069	1665 vw		1656 vw	1217 m		1025 s
None	0		1662 m		1220 m	1195 m	1030 s
5-MeO	0.115	1672 w		1640 w	1207 s	1042 s	1026 s
6-Br	0.232			1210 w	1194 m	1065 m	1030 s
6-I	0.276		1640 m		1200 m		1033 s
5-F	0.337				1197 s	1050 s	1036 s
7-Br	0.391		1640 m		1181 s		1040 s
7-NO ₂	0.710		1697 m		1210 m	1180 w	1052 s
1-Me	—				1201 w		1021 s
Compound							
II ^a	—	1668 vw		1654 vw	1206 vw		1000 m

^a N-Methylindoxyl oxime.

 TABLE IV
 REMAINING FREQUENCIES BELOW 1200 CM.⁻¹ CLASSIFIED WITH SUBSTITUTION PATTERNS

Compound								
	(A) 1,2-Disubstituted Benzenes							
II ^a	1154 w	1081 w	957 w	862 vw	785 vw	749 w	708 vw	660 vw
B ^b	1156 w	1080 m	981 m	858 vw	781 w	749 m	727 w	700 w
C ^c	—	1100 w	940 vw	888 vw	788 s	751 s	732 w	716 w
D ^d	1150 w	1101 m	951 w	890 w	774 w	740 w	—	663 w
	(B) 1,2,3-Trisubstituted Benzenes							
Substituent ^e								
7-Br	1140 s	886 vw	820 m	799 m	760 w	737 m	705 w	686 m
7-NO ₂	—	930 w	817 w	785 m	743 s	705 w	—	690 m
	(C) 1,2,4-Trisubstituted Benzenes							
Substituent ^e								
5-Me	1150 w	1128 vw	—	—	820 m	783 vw	737 w	670 w
5-MeO	1178 w	1130 vw	914 vw	881 w	817 m	780 w	735 m	671 w
5-F	1155 s	1114 w	928 m	890 m	833 m	784 m	738 m	672 w
6-Me	1153 m	1124 m	951 vw	873 vw	822 m	788 w	738 w	—
6-Br	—	1115 m	910 m	864 w	822 m	780 vw	760 w	693 w
6-I	—	1121 m	903 m	865 w	821 m	—	760 w	685 w

^a N-Methylindoxyl oxime. ^b N-Methylisatin oxime. ^c Isatin oxime. ^d Isatin. ^e All these compounds are substituted isatin oximes.

increased strength of the hydrogen bonding in the latter compounds.

Most peaks below 1180 cm.^{-1} are produced by vibrations involving the basic ring skeleton and the attached hydrogen atoms. These frequencies appear to be primarily related to the substitution pattern and are less dependent on the type of substituents. This is shown in Table IV in which, for convenience, these substances are classified as substituted benzenes in terms of their substitution type.

EXPERIMENTAL

Spectra were obtained in potassium bromide disks because

of the insolubility of most of the compounds in suitable solvents. The instrument used was a Perkin-Elmer 21 double-beam recording spectrometer with a rock-salt prism.

Compounds. Substituted isatin oximes were prepared from the corresponding isatins⁶⁻⁸ in the usual way.

N-Methylindoxyl oxime. N-Methyl-O-acetylindoxyl was dissolved in excess hot 2*N* sodium hydroxide under nitrogen. Sufficient aqueous hydroxylamine hydrochloride was then added to neutralize the solution. The oxime, m.p. 208° , was collected and crystallized from aqueous ethanol.

LONDON, ENGLAND

(6) P. W. Sadler, *J. Org. Chem.*, **21**, 169 (1956).

(7) P. W. Sadler and R. L. Warren, *J. Am. Chem. Soc.*, **78**, 1251 (1956).

(8) D. G. O'Sullivan and P. W. Sadler, *J. Chem. Soc.*, 2202 (1956).

[CONTRIBUTION FROM THE PHYSICAL RESEARCH LABORATORY AND THE SPECTROSCOPY LABORATORY,

THE DOW CHEMICAL COMPANY]

Evidence for Esters of *Aci*-Nitrocyclohexane as Intermediates in Production of Cyclohexanone Oxime

ROBERT E. MCCOY AND ROLAND S. GOHLKE

Received November 28, 1955

Processes yielding cyclohexanone oxime by reactions of *aci*-nitrocyclohexane salts with an alcohol and an acid and with an alkyl halide were recently disclosed. It is proposed that these reactions proceed *via* an unstable ester of *aci*-nitrocyclohexane. To test this hypothesis, salts of *aci*-nitrocyclohexane were treated with alkyl sulfates. As anticipated, cyclohexanone oxime was the principal product. Attempts to isolate the esters in these reactions have failed. Titrimetric data suggest that the reaction of *aci*-nitrocyclohexane with alcohols is esterification. Only three types of reagents are known to convert *aci*-nitrocyclohexane or its salts to cyclohexanone oxime; in each case an ester of *aci*-nitrocyclohexane is a logical intermediate.

Hamann and Bauer obtained cyclohexanone oxime and an aldehyde or ketone by reaction of nitrocyclohexane with a base and a primary or secondary alkyl halide.¹ Welz and Weise obtained oximes, especially cyclohexanone oxime, by gradual addition of salts of the corresponding nitroparaffins to acidified alcohols.²

It is proposed here that the path of reaction in the first case involves formation of a salt of *aci*-nitrocyclohexane, its conversion to an ester of *aci*-nitrocyclohexane by reaction with the alkyl halide, and the rapid decomposition of this unstable ester to give cyclohexanone oxime and a carbonyl compound. In the second case it is proposed that the path of reaction involves formation of the *aci*-nitro compound on addition of the salt to the acid medium, esterification of the *aci* form, and decomposition of the ester.³ If these hypotheses are

correct, it follows that reaction of salts of *aci*-nitrocyclohexane with alkyl sulfates, which should effect alkylation of the *aci* form, will also produce cyclohexanone oxime.

It was found, as predicted, that reaction of methyl or ethyl sulfate with the sodium, potassium, or calcium salt of *aci*-nitrocyclohexane yielded cyclohexanone oxime as the principal product. Yields as high as 76% were obtained by reaction of methyl sulfate with the sodium salt of *aci*-nitrocyclohexane in methanol.

In an attempt to obtain further evidence that the esters of *aci*-nitrocyclohexane are intermediates in the production of cyclohexanone oxime, this reaction and those of the prior authors^{1,2} were repeated at 0° and at dry-ice temperature. It was hoped to retard decomposition of the ester sufficiently to permit its detection, but this was not realized.⁷

Dilute solutions of *aci*-nitrocyclohexane salts in

(1) Hamann and Bauer, German Patent 825,547 (1951).

(2) Welz and Weise, German Patent 837,692 (1952).

(3) The suggested path of reaction is similar to that observed with certain nitro compounds⁴⁻⁶ in which the C=N bond of the *aci* form is conjugated with at least one benzene ring or multiple bond. In these cases both the *aci* form and the ester are generally sufficiently stable that their identification is relatively simple, in distinct contrast to the corresponding derivatives of nitrocyclohexane.

(4) Bamberger, *Ber.*, **34**, 589 (1901).

(5) Nenitzescu and Isacescu, *Ber.*, **63**, 284 (1930); *Bull. Chem. Soc. Rom.*, **14**, 53 (1932).

(6) Arndt and Rose, *J. Chem. Soc.*, **1**, (1935).

(7) This failure may have been due to lack of analytical equipment designed for operation below room temperature. The samples could be kept cold only until the analytical instruments were loaded.