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The Structure of Salts of β-Dione Dioximes

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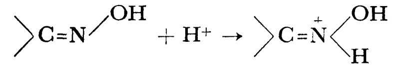
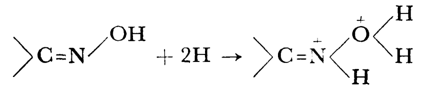
Cyclohexane-1,3-dione dioxime hydrochloride was prepared and investigated with reference to its structure. Analysis and a study of its NMR and IR spectra suggested that the salt is the enamine form of the oxime. Further, the salts of 5-methylcyclohexane-1,3-dione dioxime, 5,5-dimethylcyclohexane-1,3-dione dioxime and acetylacetone dioxime were prepared and found to have the same structure.

For the structure of ketoxime salt, the structure of cyclohexanone oxime hydrochloride was investigated by Saito.[1] The proton was known to be attached to the nitrogen of the hydroxyimino group as in Eq. (1). Further, an excess of strong acid was found to make another kind of salt containing two molecules of acid. Here, protons bond with the nitrogen and the oxygen of oxime as in Eq. (2). The salt with two molecules of acid, however, is so unstable that it easily releases one molecule of hydrogen chloride at room temperature.



$$ {>}C{=}N{-}OH + H^+ \rightarrow {>}C{=}\overset{+}{N}{<}^{OH}_{H} \qquad (1)$$



$$ {>}C{=}N{-}OH + 2H \rightarrow {>}C{=}\overset{+}{N}{<}^{\overset{+}{O}{<}^{H}_{H}}_{H} \qquad (2)$$

In our series of studies to synthesize cyclic diamides, the Beckmann rearrangement of the dioximes of alicyclic diones has been carried out. During the study of the rearrangement, the characteristic structures of the salts of β-dione dioximes were found. β-Dione dioxime gave only one kind of stable salt, with one molecule of hydrogen chloride, in spite of the presence of two hydroxyimino groups. In the present study, the structure of the salt of β-dione dioxime will be discussed on the basis of a study of the NMR and IR spectra.

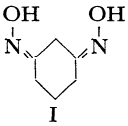
Results and Discussion

The β-dione dioximes were derived from β-diones according to the usual method. The β-diones used as starting materials were cyclohexane-1,3-dione, 5-methylcyclohexane-1,3-dione, 5,5-dimethylcyclohexane-1,3-dione and acetylacetone. The salts of these β-dione dioximes were obtained as crystals on adding various acids in acetic acid solutions. The results are summarized in Table 1, along with the data of elementary analyses.

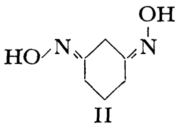
Cyclohexane-1,3-dione dioxime was expected to act as a diacid base. An elementary analysis of the salt, however, showed that the salt contains only one molecule of hydrogen chloride. Even if an excess of hydrogen chloride was added, dihydrochloride was not obtained.

Since the results obtained seemed to be anomalous, a further attempt to prepare various salts of β-dione dioximes was made to confirm that β-dione dioximes act as monoacid bases. In every case here, the salts of β-dione dioximes contained an equivalent of acid. The addition of a half mole of sulfuric acid to 1 mol of cyclohexane-1,3-dione dioximes gave a quantitative yield of the salt; this salt, on the addition of another half mole of sulfuric acid, dissolved in acetic acid again, we could not isolate the product. For the sake of comparison, we studied how to obtain γ-dione dioxime monohydrochloride by the same method, but in the case of cyclohexane-1,4-dione dioxime, monohydrochloride was not obtained, rather, hygroscopic crystals of dihydrochloride were precipitated by the addition of an excess of hydrochloric acid. In view of the above facts, the salts of β-dione dioximes seemed to have structures different from those of the salts of the other oximes such as cyclohexanone oxime.

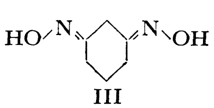
The Structure of 5,5-Dimethylcyclohexane-1,3-dione Dioxime. As a structure of cyclohexane-1,3-dione dioxime, the presence of three kinds of isomers were proposed, as is shown below:



I



II



III

Here, in the NMR spectrum of the dioxime, methylene protons at the 2 position gave three peaks

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1) H. Saito, *Nippon Kagaku Zasshi*, **85**, 728 (1964).

Table 1. Salts of β-dione dioximes and elementary analyses

Dioxime	Acid HX	Method	Yield (%)	Mp (°C)	Elementary analyses		
					C (%)	H (%)	N (%)
Cyclohexane-1,3-dione dioxime	HCl	A	100	190 (d)	C. 40.34	6.21	15.68
					F. 40.20	5.92	15.17
	$\frac{1}{2}H_2SO_4$	A	100	180 (d)	C. 37.70	5.80	14.62
					F. 37.80	5.87	13.80
	$CH_3C_6H_4SO_3H$	A	66	180—180.5	C. 49.68	5.54	8.91
					F. 49.27	5.77	9.08
	$C_6H_2(NO_2)_3OH$	B	60	166—167	C. 38.92	3.53	18.87
					F. 38.55	3.54	19.54
5-Methylcyclohexane-1,3-dione dioxime	HCl	B	80	179 (d)	C. 44.00	6.83	14.69
					F. 43.64	6.80	14.54
5,5-Dimethylcyclohexane-1,3-dione dioxime	HCl	B	81	177—178	C. 46.50	7.24	13.57
					F. 47.02	7.40	13.92
Acetylacetone dioxime	$\frac{1}{2}H_2SO_4$	B	50	104—105	C. 33.33	6.21	15.27
					F. 33.52	6.19	15.64

d: decomposition C.: Calcd for dioxime·HX F.: Found Method A and B: *cf.* experimental

corresponding to the protons of the structures I, II, and III, while the methylene protons at the 4, 5, and 6 positions gave very complicated signals.[2] In the present study the NMR spectrum of 5,5-dimethylcyclohexane-1,3-dione dioxime was found to give a rather simple chart, as is shown in Fig. 1, because the carbon at the 5 position has no hydrogen.

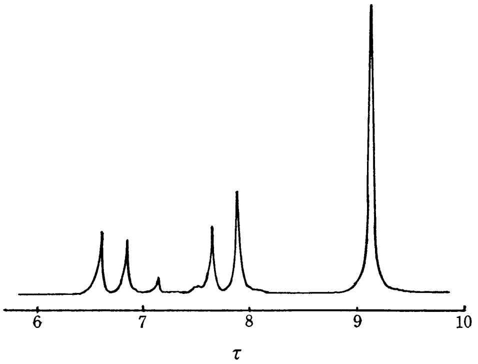

Fig. 1. NMR spectrum of 5,5-dimethylcyclohexane-1,3-dione dioxime. (DMSO-d_6 60MHz)

The methylene protons at the 2 position are observed around τ 6.5—7.2 as three signals. The central signal of these three can be assigned to the structure II analogous to results previously reported.[2] The assignment of the other two signals, one of which corresponds to the syn-syn or anti-anti form, has not been made. The ratio of the intensities of the three signals of the methylene protons at the 2 position in 5,5-dimethylcyclohexane-1,3-dione dioxime is 6 : 3 : 1.

The signals of the methylene protons at the 4 and 6 position are observed as two peaks around τ 7.5—8.0. These seemed to correspond to syn and anti protons with respect to the hydroxyimino group. The protons at the 4- and 6-methylene of Form I are all anti protons, and those of Form III are all syn; moreover in Form II either the protons of 4-methylene or those of 6-methylene are syn, and the other are anti protons. Finally, without regard to the differences between Forms I, II, and III, the methylene protons at the 4 and 6 positions are divided into just two classes. From the ratio of the intensities of the signals of 2-methylene, the ratio of syn and anti protons at 4- and 6-methylenes, was calculated to 1 : 3. This calculated value coincides with the experimental result. The separation between the two peaks indicates the difference in the shielding constants of the syn and anti protons. The value obtained is 0.24 ppm, which is expected to be consistent with the separations between both side peaks and the central one of 2-methylene; however, the actual values related to 2-methylene are 0.24 and 0.29 ppm. A further, detailed discussion of this point is required.

NMR Spectra of Salts of β-Dione Dioximes. The NMR spectra of the β-dione dioxime monohydrochlorides are shown in Fig. 2.

If the structure of the salt of β-dioxime is IV, as is expressed in Eq. (3), in which the proton is attached to one of the two nitrogens, the signal of the methylene protons between the two oxime groups would shift toward a lower field by about 0.3 ppm because of the influence of protonated oxime, as has been indicated by Saito, and the signal would be observed as a doublet due to the anisotropic effect of the syn and anti forms of the oxime group which was not protonated. The spectrum actually obtained, however, gave a quite

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2) H. Saito and K. Nukada, *Tetrahedron Lett.*, **1965**, 2117.

3) H. Saito, *J. Mol. Spectrosc.*, **18**, 355 (1965).

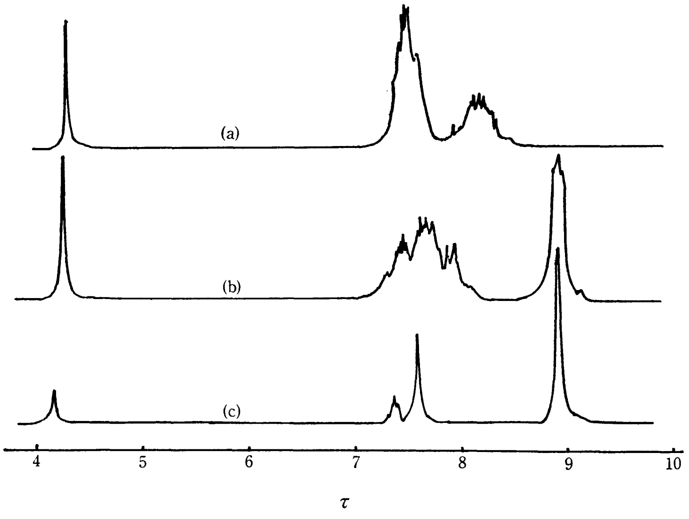
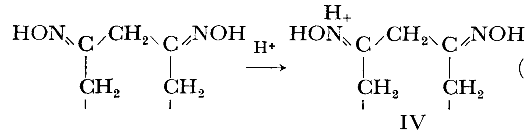


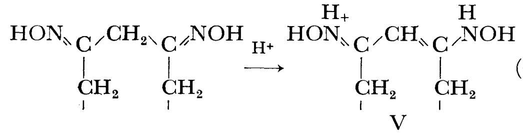
Fig. 2. NMR spectra of cyclohexane-1,3-dione dioxime hydrochloride (a), 5-methylcyclohexane-1,3-dione dioxime hydrochloride (b), 5,5-dimethylcyclohexane-1,3-dione dioxime hydrochloride (c), (DMSO-d_6 60MHz).

different figure from that assumed from the above consideration.

 (3)

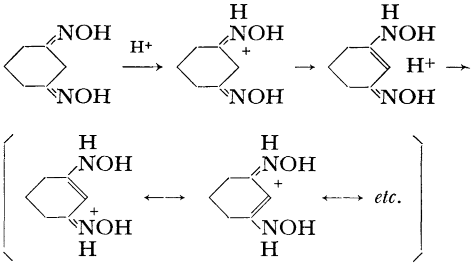
$$\mathrm{HON{=}\underset{\displaystyle CH_2}{C}\text{-}CH_2\text{-}\underset{\displaystyle CH_2}{C}{=}NOH \xrightarrow{H^+} \overset{H^+}{HON}{=}\underset{\displaystyle CH_2}{C}\text{-}CH_2\text{-}\underset{\displaystyle CH_2}{C}{=}NOH} \quad \text{IV} \qquad (3)$$

The methylene signals which have been observed in 5,5-dimethylcyclohexane-1,3-dione dioxime around τ 6.5—7.2, disappear completely, and a new signal is found at about τ 4. Further, the same phenomenon is observed in each of our experiments. The number of the proton which gave the signal at τ 4 is estimated by comparison with those of the other methylene or methyl protons to be one. Therefore, it is reasonable to consider that the structure of β-dione dioxime changes from the imine form to the enamine form V by means of salt formation, as is shown in Eq. (4):

 (4)

$$\mathrm{HON{=}\underset{\displaystyle CH_2}{C}\text{-}CH_2\text{-}\underset{\displaystyle CH_2}{C}{=}NOH \xrightarrow{H^+} \overset{H^+}{HON}{=}\underset{\displaystyle CH_2}{C}\text{-}CH{=}\underset{\displaystyle CH_2}{C}\text{-}\overset{H}{N}OH} \quad \text{V} \qquad (4)$$

It is well known that β-diketone exists mainly as an enol form, while β-dione dioxime does not take an enamine form. This is interpreted as being due to the difference in electron-withdrawing tendencies between carbonyl and oxime groups. If β-dione dioxime is protonated, the electron-withdrawing character of the oxime will increase very much and the hydrogens of methylene between the two oxime groups will become acidic. Consequently, the salt of β-dione dioxime will have a structure of an enamine, as is shown in Eq. (5):

 (5)

This resonance stabilization can explain how the β-dione dioxime acts as a monoacid base. The structure described above is also supported by the fact that the protons of the 4 and 6 positions of 5,5-dimethylcyclohexane-1,3-dione dioxime hydrochloride show a single signal.

IR Spectra of the Salts. The absorption band of the carbon nitrogen double bond of cyclohexanone oxime (1669 cm^{-1}) was reported to shift to the higher-wave-number region of 1696 cm^{-1} upon salt formation.[1] However, 5,5-dimethylcyclohexane-1,3-dione dioxime gave just the opposite result.

The IR spectra of 5,5-dimethylcyclohexane-1,3-dione dioxime and its hydrochloride are illustrated in Fig. 3. The absorption at 1655 cm^{-1} shifts to the lower-wave-number region of 1578 cm^{-1} upon salt formation. Further, a new absorption, which seems to be attributable to a C=C double bond, appears at 1610 cm^{-1}. Some bands of the IR absorptions of various β-dione dioximes and other oximes, and of these hydrochlorides, are shown in Table 2.

If the structure of the salt of β-dione dioxime were IV, in which the proton is added to one nitrogen of the two hydroxyimino groups, two peaks related to C=N and C=N^+ streching would

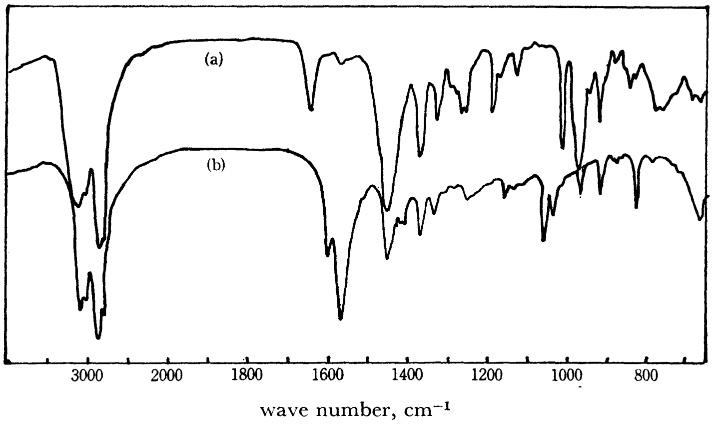


Fig. 3. IR spectra of 5,5-dimethylcyclohexane-1,3-dione dioxime (a) and its hydrochloride (b).

TABLE 2. INFRARED ABSORPTION FREQUENCIES OF THE DIOXIMES AND THEIR SALTS (cm^{-1})

	Dioximes		The oxime hydrochlorides		
	OH	C=N	OH	N$^+$H	C=N$^+$
Cyclohexane-1,3-dione dioxime	3200, 3100	1665	3200, 3100	3000—2500	1595
5-Methylcyclohexane-1,3-dione dioxime	3200, 3080	1655	3140, 3080	3000—2500	1582
5,5-Dimethylcyclohexane-1,3-dione dioxime	3200, 3080	1655	3150, 3070	3000—2500	1578
Acetylacetone dioxime	3200, 3100	1670	3200, 3100	2650	1610
Cyclohexane-1,4-dione dioxime	3200, 3100	1665	3300	2600	1710
Cyclohexanone oxime	3190, 3110	1650	3350	2600	1695

appear. In the case of the structure V, the resonance of C=N$^+$ and C=N can explain why the peak shifts to a low-frequency region and the intensity is very strong. Therefore, the experimental results of the IR absorption spectra seem to support the structure V, too.

The wave number of the carbon-nitrogen stretching of the salt of β-dione dioxime varies with the number of methyl groups at the 5 position. The chemical shift of the methine proton of the salt varies also, as is shown in Table 3. These differences seem to have some correlation with the change of the conformation of the ring, though this question has not yet been elucidated.

TABLE 3. THE CHEMICAL SHIFTS OF THE METHINE PROTON AND IR ABSORPTION FREQUENCIES OF CN$^+$ STRETCHING OF THE DIOXIME HYDROCHLORIDES

	τ (ppm)	C=N$^+$ (cm^{-1})
Cyclohexane-1,3-dione dioxime hydrochloride	4.28	1595
5-Mthylcyclohexane dioxime hydrochloride	4.26	1582
5,5-Dimethylcyclohexane-1,3-dione dioxime hydrochloride	4.15	1578

Experimental

The cyclohexane-1,3-dione,[4] 5-methylcyclohexane-1,3-dione,[5] and 5,5-dimethylcyclohexane-1,3-dione[6] were synthesized by the methods given in the literature. The acetylacetone was obtained from a commercial source. The dioximes of these diones were prepared by the usual method.

Cyclohexane-1,3-dione Dioxime Hydrochloride. Cyclohexan-1,3-dione dioxime was dissolved in acetic acid. An equivalent weight of concentrated hydrochloric acid was added to the solution, and then the hydrochloride was precipitated. The hydrochloride was reprecipitated from methanol by the addition of ether (Method A).

5-Methylcyclohexane-1,3-dione Dioxime Hydrochloride. 5-Methylcyclohexane-1,3-dione dioxime was dissolved in acetic acid. After the addition of an equivalent weight of hydrochloric acid, a small amount of ether was added, and then hydrochloride was precipitated (Method B).

Other salts of the dioximes were prepared by the method A or B, as is shown in Table 1.

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[4] R. B. Thompson, "Organic Syntheses," Coll. Vol. III, p. 279 (1955).

[5] A. W. Crossley, *J. Chem. Soc.*, **107**, 602 (1915).

[6] R. L. Shriner and H. R. Todd, "Organic Syntheses," Coll. Vol. II, p. 200 (1948).