166. Kentaro Hiraga : Structures of Cyclopentanepolyones.

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Chart 1.

It is known that 1,2-cyclopentanediol exists almost entirely in enol-ketone form (I).¹⁾ Recently, 2-acetyl-1,3-cyclopentanediol has been found to take the monoenolic formula (II).²⁾

On the occasion of the syntheses of cyclopentanepolyones as reported in the previous paper,³⁾ the author had a chance to examine their physicochemical behaviors and structures. Here, the cyclopentanepolyones were classified into several groups, namely, 1,3-diones, 1,2,4-triones and their derivatives, and the discussions were mainly based on the results of physicochemical measurements.

1,3-Cyclopentanediolones

Prof. Woodward⁴⁾ pointed out already that 2-ethyl-4-propyl-1,3-cyclopentanediolone would be present as the hybrid anion (III) in the alkaline solution.

Chart 2.

TABLE I. Infrared Absorption Spectra of 2-Substituted
1,3-cyclopentanediolones (IV) (in Nujol)

Compounds R	Hydroxyl	Conjugated carbonyl	Conjugated and chelated carbonyl
H	2400		1560
CH ₃	2620	1690	1575
C ₂ H ₅	2500	1680	1550
iso-C ₃ H ₇	2500	1660	1550
	2500	1670	1550
CH ₂ -	2600	1680	1568

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1) G. Schwarzenback, C. Wittwer : *Helv. Chim. Acta*, **30**, 663 (1947).2) M. Vandwalle : *Bull. Soc. Chim. Belg.*, **73**, 628 (1964).3) K. Hiraga : *This Bulletin*, **13**, 1359 (1965).4) R. B. Woodward, E. R. Blout : *J. Am. Chem. Soc.*, **65**, 562 (1943).

The author first examined the infrared spectra of 1,3-cyclopentanediones (IV) as well as cyclopentene-1,3-dione (V) and methyl ether of 2-methyl-1,3-cyclopentanedione (VI) (see Table I and Fig. 1). The spectrum of cyclopentene-1,3-dione (V) showed a conjugated carbonyl band at 1700 cm^{-1} but no hydroxyl band was observed in the spectrum, indicating that V exists in diketonic form. The absorption at 1670 cm^{-1} exhibited by methyl ether (VI) was assigned to the carbonyl group which is conjugated with the enol ether group. On the other hand, the spectra of 1,3-cyclopentanediones (IV) showed two characteristic bands in the $1550\sim 1580\text{ cm}^{-1}$ region and in $2300\sim 2700\text{ cm}^{-1}$ region. The former, being very strong and broad, may be attributed to a conjugated and chelated carbonyl group, and the latter to a strongly hydrogen bonded hydroxyl group. Besides, the weak band at $1680\sim 1700\text{ cm}^{-1}$ that always appears in IV suggests the existence of some non-chelated carbonyl groups probably at the terminal position of the associated complex or on the monomeric molecule. These observations indicate that IV is present as the polymeric enol-ketone from (VII) at least in the crystalline state.

Fig. 1. Infrared Absorption Spectrum of 2-Methyl-1,3-cyclopentanedione (IV, R=CH₃) (in Nujol)

Chart 3.

As for dimedone, a dimeric form (VIII) was postulated by Prof. Nakanishi.⁵⁾ But an analogous form cannot be considered since the two characteristic bands appear irrespective of the substituent at carbon-2.

The nuclear magnetic resonance spectra (Table II) also support the structures proposed above. The spectrum of cyclopentene-1,3-dione (V) showed the presence of a methylenic and an olefinic proton in the same intensity, and the diketonic form for V was confirmed again.

The spectrum of the methyl ether (VI), unexpectedly, showed a triplet ($J=1.5\text{ c.p.s.}$) for the 2-methyl group and an asymmetric multiplet for the methylene group, suggesting the presence of a long range coupling between 2-methyl protons and the methylene protons at either carbon-4 or carbon-5. In the spectra of 1,3-cyclopentanediones (IV), no signal was observed at the field expected (ca. 3.0 p.p.m. (δ)) for the active hydrogen between the two carbonyl groups, and the methyl signal in 2-methyl-1,3-cyclopentanedione (IV, R=CH₃) and the benzyl signal in 2-benzyl-1,3-cyclopentanedione (IV, R=CH₂-) appeared as singlet, suggesting that IV exists entirely in the enolic form (IX) or the corresponding anion in pyridine solution. Since the olefinic proton (5.48 p.p.m.) in the spectrum of 1,3-cyclopentanedione (IV, R=H) disappeared on

5) K. Nakanishi: "IR Absorption Spectroscopy-Practical," p. 69 (1962), Nankodo Co., Tokyo.

TABLE II. Nuclear Magnetic Resonance Spectra of 1,3-Cyclopentanediones (IV) (δ)

Compounds	H ^a	H ^b	H ^c	H ^d	Solvent
2.92 s	7.34 s			CDCl ₃
2.6, 2.3 m		1.54 t	3.94 s	CCl ₄
2.51 s 2.61 s	5.48 s			pyridine pyridine + D ₂ O
2.48 s 2.48 s		1.89 s 1.59 s		pyridine MeOH
2.42 s		3.79 s		pyridine

s: singlet t: triplet m: multiplet

addition of deuterium oxide, the enolic form (K) is considered not to be fixed at all. Moreover, the four methylenic protons in IV were found to be equivalent in nuclear magnetic resonance spectra: this proves quick tautomerism between the two enolic forms (K and K').

Fig. 2. Ultraviolet Absorption Spectra of 2-Ethyl-1,3-cyclopentanedione (IV, R=C₂H₅)

— neutral - - - - pH 1
- · - · - pH 10

The ultraviolet absorptions of 1,3-cyclopentanediones (IV) showed maxima at around 250 mμ in neutral and acidic solutions, and they shifted to near 270 mμ in the alkaline solution (see Table III and Fig. 2). The maxima at (about) 250 mμ must be due to the enolic forms (K) since the spectrum of the enol ether (V) showed the maximum at the same wave length (250 mμ). The absorption spectrum of cyclopentene-1,3-dione (V) showed a maximum at 220 mμ in neutral and acidic solutions and at 262 mμ in the alkaline solution: the latter indicates that V exists in enol-anionic form (X) in the basic circumstances.

1,3-Cyclopentanediones (IV) are strong acids, like acetic or propionic acid, and the pK values measured by potentiometric titration are given in Table IV.

TABLE III. Ultraviolet Absorption Maxima of 1,3-Cyclopentanediones (IV) ($m\mu$, ϵ)

Compounds R	pH 1	Neutral	pH 10
H	244 1.0×10^4	249 9.8×10^3	269 1.4×10^4
CH ₃	253 1.75×10^4	251 1.66×10^4	271 2.57×10^4
C ₂ H ₅	253 1.6×10^4	250 1.58×10^4	271 2.54×10^4
iso-C ₃ H ₇	253 1.6×10^4	251 1.57×10^4	271 2.54×10^4
257 1.42×10^4	
CH ₂ -		246 1.6×10^4	
VI		250 1.6×10^4	

TABLE IV. pK of 1,3-Cyclopentanediones (IV) and 1,2,4-Cyclopentanetriones (XI)

R
	pK	solvent	pK	solvent
H	4.4	H ₂ O		
CH ₃	4.7	"	3.4	H ₂ O
C ₂ H ₅	4.7	"	3.5	"
iso-C ₃ H ₇	5.1	"	3.5	"
5.4	50% EtOH		
CH ₂ -	5.7	"	5.2	"

1,2,4-Cyclopentanetriones

The infrared spectra of these compounds measured by the Nujol mull method had three absorptions at 3470, 3150, and 2680 cm^{-1} in the region of hydroxyl stretching frequency. But when they were measured in a dilute carbon tetrachloride solution (5.1 mg. in 50 ml.), the two absorptions at 3150 and 2680 cm^{-1} disappeared, remaining the absorption at 3470 cm^{-1} , which must be due to a stretching of an intramolecularly hydrogen bonded hydroxyl group (see Fig. 3). The nuclear magnetic resonance spectra

Fig. 3. Infrared Absorption Spectra of 3-Methyl-1,2,4-cyclopentanetrione (XI, R=CH₃)a: in Nujol b: in CCl₄ (5.1 mg./50 ml.)

of these compounds (XI) are shown in Table V. They showed the methylene signal at 2.9~2.98 p.p.m. as singlet, and gave no signal of olefinic proton which would appear around 5.48 p.p.m. Both the methyl signal in 3-methyl-1,2,4-cyclopentanetrione (XI, R=CH₃) and the benzyl signal in 3-benzyl-1,2,4-cyclopentanetrione (XI, R=CH₂-)

TABLE V. Nuclear Magnetic Resonance Spectra of 1,2,4-Cyclopentanetriones (XI) (in CDCl_3 , δ)

Compounds	H^a	H^b	H^c
3.01 s	1.98 s
2.93 s	2.48 q	1.17 t
2.91 s	3.71 s	7.23 s

s: singlet t: triplet q: quartet

Chart 4.

appeared as a singlet. These facts indicate that, of the two possible enolic forms (XII and XIII) the former may be preferable.*²

The ultraviolet absorptions of the triones (XI) showed maxima at around 278 $\text{m}\mu$ in neutral and acidic solutions, and they shifted to near 326 $\text{m}\mu$ in the alkaline solution.

The formers are attributed to the enol forms (XII) and the latters to enol anions (see Fig. 4).

The triones (XI) are stronger acid than the diones (IV), and the pK values measured by potentiometric titration are given in Table IV.

Semicarbazones of 1,2,4-Cyclopentanetriones

Since the semicarbazones were not soluble in the organic solvent, their infrared absorptions were measured by the Nujol mull method. It was interesting to note that the spectra showed strong absorption at 1750 cm^{-1} without exception (see Fig. 5). On the other hand, in the spectra of the oxime, phenylhydrazone and butyroylhydrazone

*² Although the structure was not decided conclusively, E. Leucht and W. Riedl proposed the two enolic forms (XII and XIII) for the 3-alkyl-1,2,4-cyclopentanetrione (XI). (Ann., 669, 55 (1963))

of 1,2,4-cyclopentanetriones, no absorption was observed in the $1700\sim 1750\text{ cm}^{-1}$ region: this indicates that one of the two oxo-groups in these compounds exists in enolic form (see XIV). Though the assignment of the absorption at 1750 cm^{-1} is not established yet, it may be reasonable to postulate an intramolecular hydrogen bonding as is shown in XV.

Fig. 5. Infrared Absorption Spectrum of 3-Methyl-1,2,4-cyclopentanetrione Semicarbazone (XV) (in Nujol)

Chart 5.

Ethyl 2,4,5-Trioxocyclopentylglyoxylates

In the infrared spectra of the glyoxylates in a dilute carbon tetrachloride solution (5.8 mg. in 50 ml.), the stretching absorption of the hydroxyl group appeared at 3447 cm^{-1} , suggesting the presence of an intramolecular hydrogen bonding.*³

Fig. 6. Nuclear Magnetic Resonance Spectrum of Ethyl 3-Benzyl-2,4,5-trioxocyclopentylglyoxylate (XVI, $R=\text{CH}_2-\text{C}_6\text{H}_5$) (in CDCl_3)

Fig. 7. Ultraviolet Absorption Spectra of Ethyl 3-Ethyl-2,4,5-trioxocyclopentylglyoxylate (XVI, $R=\text{C}_2\text{H}_5$)
— neutral - - - pH 1
· · · pH 10

The nuclear magnetic resonance spectrum of ethyl 3-benzyl-2,4,5-trioxocyclopentylglyoxylate measured in deuteriochloroform showed a singlet peak at 3.71 p.p.m. (δ) for the benzyl proton (see Fig. 6), and no signal corresponding to the proton attached to

Chart 6.

*³ In Nujol, the stretching absorption of hydroxyl group was observed at $3100\sim 3200\text{ cm}^{-1}$, whereas no absorption appeared in the $2300\sim 2800\text{ cm}^{-1}$ region where the strong absorption was observed in the case of the 1,3-cyclopentanediones (N). This might suggest the absence of intermolecular hydrogen bonding in the glyoxylates.

the ring carbon was observed. Because of the low solubility in organic solvents of other derivatives in this group, their nuclear magnetic resonance spectra were not measured.

The ultraviolet absorption spectra of the glyoxylates showed curves (see Fig. 7) quite different from those of the triones (XI).

All these facts indicate the glyoxylates exist in the extremely enolic form, and the most plausible formula among the three (XVI, XVII, XVIII) may be XVI, since this would be thermodynamically the most stable.

Experimental*4

Most of the materials used in this work were prepared by the method described in the preceding paper.

The oxime, the phenylhydrazone and the butyroylhydrazone were prepared from 3-methyl-1,2,4-cyclopentanetrione (XI, R=CH₃).

Oxime m.p. 238°, *Anal.* Calcd. for C₆H₇O₃N: C, 51.06; H, 4.96; N, 9.92. Found: C, 50.77; H, 4.96; N, 9.75.

Phenylhydrazone m.p. 238°, *Anal.* Calcd. for C₁₂H₁₂O₂N₂: C, 66.67; H, 5.56; N, 12.96. Found: C, 66.78; H, 5.50; N, 13.00.

Butyroylhydrazone m.p. 224°, *Anal.* Calcd. for C₁₀H₁₄O₃N₂: C, 57.14; H, 6.67; N, 13.33. Found: C, 56.98; H, 6.64; N, 13.29.

Methyl Ether of 2-Methyl-1,3-cyclopentanedione (VI)—To a suspension of 1 g. of 2-methyl-1,3-cyclopentanedione (IV, R=CH₃) in 50 ml. of tetrahydrofuran was added an excess amount of an ether solution of diazomethane under ice cooling, and the mixture was allowed to stand in a refrigerator for 1 hr.

After evaporation of the solvent, the oily residue was distilled under reduced pressure. The fraction at 70~142°/26 mm. which solidified on standing was recrystallized from hexane to give 0.5 g. of colorless crystals, m.p. 68°. *Anal.* Calcd. for C₇H₁₀O₂: C, 66.67; H, 7.93. Found: C, 66.40; H, 7.98.

Apparatus

The IR spectra in Nujol mull were obtained using a Hitachi EPI-S₂ spectrophotometer, and those in carbon tetrachloride were measured with a Parkin-Elmer model 221 spectrophotometer.

The UV spectra were recorded with a Hitachi EPS-2 recording spectrophotometer.

The NMR spectra were measured with a Varian A-60 spectrometer at 60 Mc. (δ-value).

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Summary

Based on the results of physicochemical measurements, the enolic forms of 1,3-cyclopentanediones (IV), 1,2,4-cyclopentanetriones (XI), semicarbazones of 1,2,4-cyclopentanetriones and ethyl 2,4,5-trioxocyclopentylglyoxylate were discussed, and the structures (IX, XII, XV, and XVI) were proposed respectively.

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*4 All melting points are uncorrected.