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166. Kentaro Hiraga : Structures of Cyclopentanepolyones.

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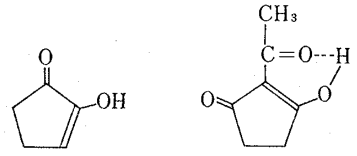

I II

Chart 1.

It is known that 1,2-cyclopentanedione exists almost entirely in enol-ketone form (I).[1] Recently, 2-acetyl-1,3-cyclopentanedione has been found to take the mono-enolic 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-Cyclopentanediones

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

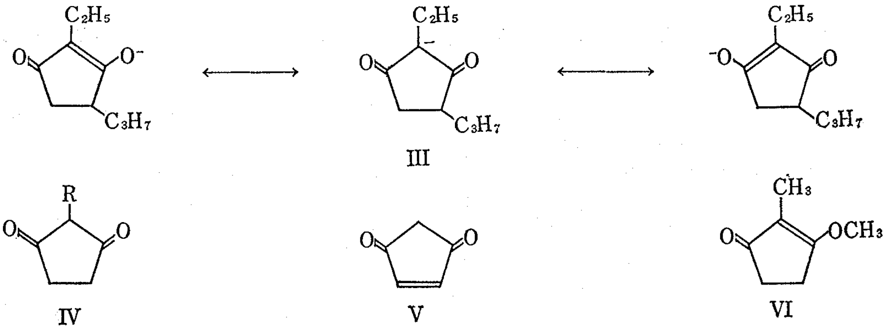
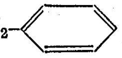


Chart 2.

Table I. Infrared Absorption Spectra of 2-Substituted 1,3-cyclopentanediones (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

[*1] Juso-nishino-cho, Higashiyodogawa-ku, Osaka (平賀謙太郎).

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).

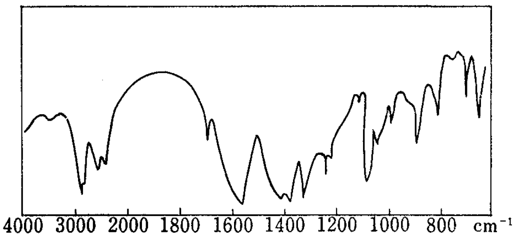


Fig. 1. Infrared Absorption Spectrum of 2-Methyl-1,3-cyclopentanedione (IV, R=CH_3) (in Nujol)

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 1550～1580 cm^{-1} region and in 2300～2700 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 1680～1700 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.

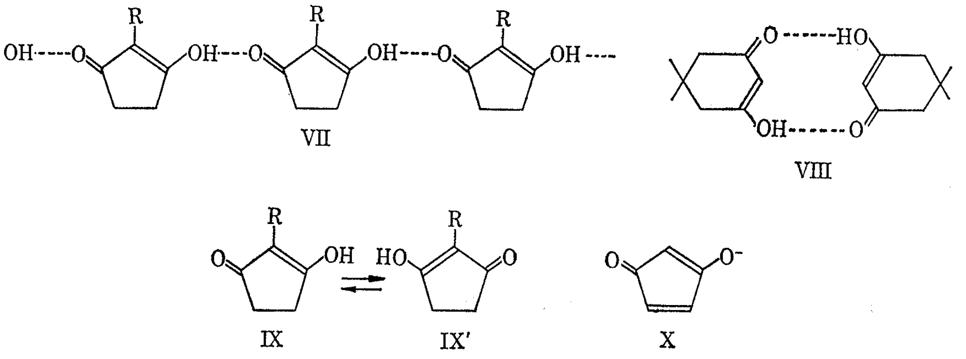
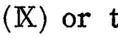


Chart 3.

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 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=CH_3) and the benzyl signal in 2-benzyl-1,3-cyclopentanedione (IV, R=CH_2-) 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

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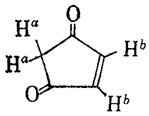
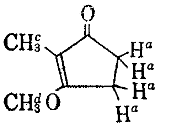
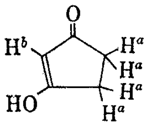
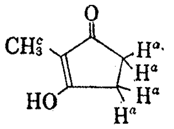
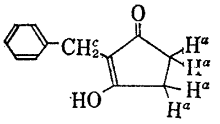
[5] K. Nakanishi: "IR Absorption Spectroscopy-Practical," p. 69 (1962), Nankodo Co., Tokyo.

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	5.48 s			pyridine
	2.61 s				pyridine + D_2O
	2.48 s		1.89 s		pyridine
	2.48 s		1.59 s		MeOH
	2.42 s		3.79 s		pyridine

s: singlet t: triplet m: multiplet

addition of deuterium oxide, the enolic form (Ⅸ) 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 (Ⅸ and Ⅸ′).

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 (Ⅸ) since the spectrum of the enol ether (Ⅵ) 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.

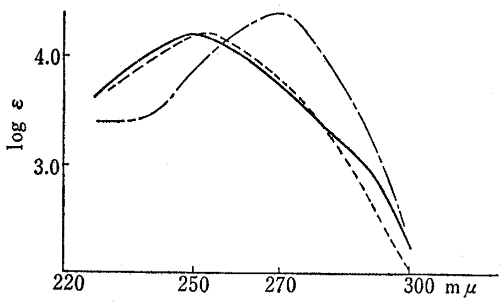


Fig. 2. Ultraviolet Absorption Spectra of 2-Ethyl-1,3-cyclopentanedione (Ⅳ, $R=C_2H_5$)

——— neutral ---- pH 1
----- pH 10

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) (mμ, ε)

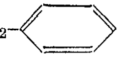
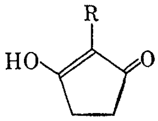
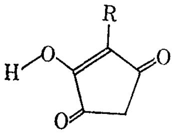
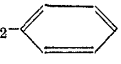
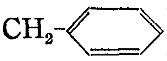
Compounds R	pH 1		Neutral		pH 10	
H	244	1.0×10^4	249	9.8×10^3	269	1.4×10^4
CH_3	253	1.75×10^4	251	1.66×10^4	271	2.57×10^4
C_2H_5	253	1.6×10^4	250	1.58×10^4	271	2.54×10^4
iso-C_3H_7	253	1.6×10^4	251	1.57×10^4	271	2.54×10^4
			257	1.42×10^4		
CH_2-			246	1.6×10^4		
VI			250	1.6×10^4		

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

				
R	pK	solvent	pK	solvent
H	4.4	H_2O		
CH_3	4.7	〃	3.4	H_2O
C_2H_5	4.7	〃	3.5	〃
iso-C_3H_7	5.1	〃	3.5	〃
	5.4	50% EtOH		
CH_2-	5.7	〃	5.2	〃

1,2,4-Cyclopentanetriones

The infrared spectra of these componuds 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 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=CH_3) and the benzyl signal in 3-benzyl-1,2,4-cyclopentanetrione (XI, R=CH_2-)

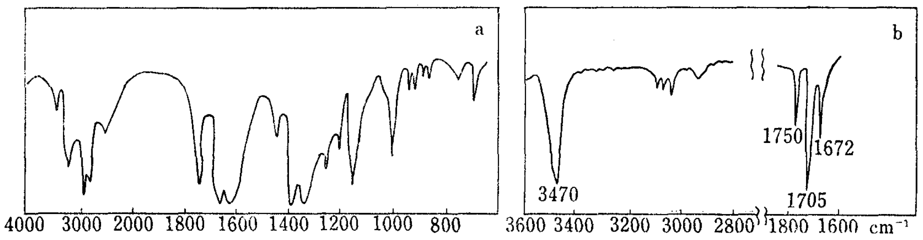
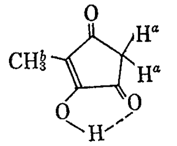
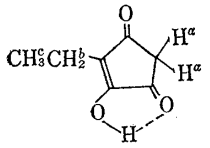
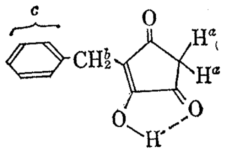


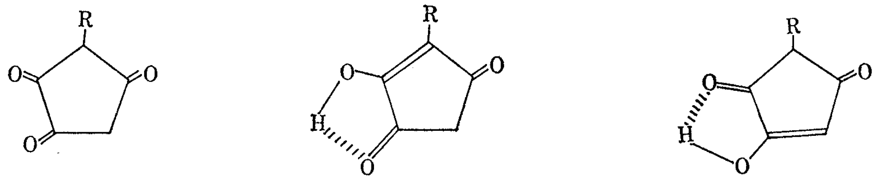
Fig. 3. Infrared Absorption Spectra of 3-Methyl-1,2,4-cyclopentanetrione (XI, R=CH_3)

a: in Nujol *b*: in CCl_4 (5.1 mg./50 ml.)

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



XI XII XIII

Chart 4.

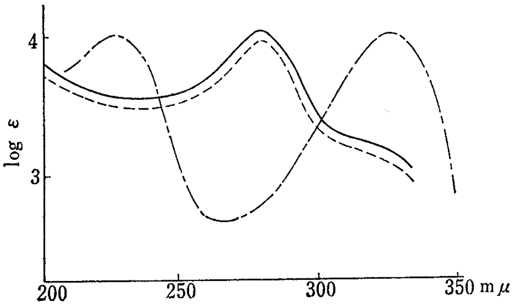


Fig. 4. Ultraviolet Absorption Spectra of 3-Ethyl-1,2,4-cyclopentanetrione (XI, $R=C_2H_5$)

——— neutral ‒ ‒ ‒ ‒ pH 1
‒·‒·‒ pH 10

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 mμ in neutral and acidic solutions, and they shifted to near 326 mμ 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

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[*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 1700~1750 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.

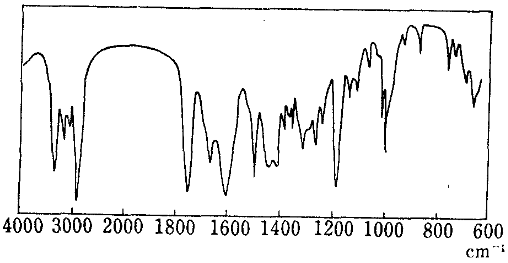
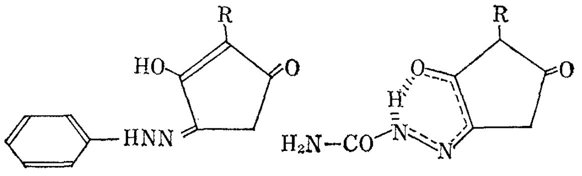


Fig. 5. Infrared Absorption Spectrum of 3-Methyl-1,2,4-cyclopentanetrione Semicarbazone (XV) (in Nujol)



XIV XV

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]

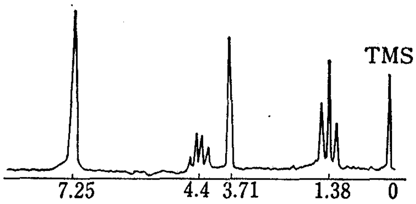


Fig. 6. Nuclear Magnetic Resonance Spectrum of Ethyl 3-Benzyl-2,4,5-trioxocyclopentylglyoxylate (XVI, R=CH_2-C_6H_5) (in $CDCl_3$)

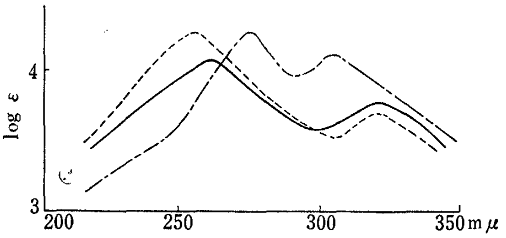
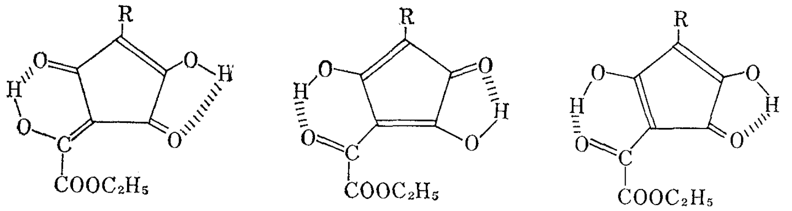


Fig. 7. Ultraviolet Absorption Spectra of Ethyl 3-Ethyl-2,4,5-trioxocyclopentylglyoxylate (XVI, R=C_2H_5)

——— neutral ---- pH 1
-·-·- pH 10

The nuclear magnetic resonance spectrum of ethyl 3-benzyl-2,4,5-trioxocyclopentylglyoxylate measured in deuterochloroform 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



XVI XVII XVIII

Chart 6.

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[3] In Nujol, the stretching absorption of hydroxyl group was observed at 3100~3200 cm^{-1}, whereas no absorption appeared in the 2300~2800 cm^{-1} region where the strong absorption was observed in the case of the 1,3-cyclopentanediones (IV). 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, $R=CH_3$).

Oxime	m.p. 238°, *Anal.* Calcd. for $C_6H_7O_3N$: 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 $C_{12}H_{12}O_2N_2$: 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 $C_{10}H_{14}O_3N_2$: 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, $R=CH_3$) 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 $C_7H_{10}O_2$: 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-S_2 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-volue).

The author wishes to express his deep gratitude to Takeda Chemical Industries, Ltd. for permission to publish this report, to Dr. Y. Abe and Dr. T. Miki for their guidance and encouragement throughout this work. He is also indebted to Mr. T. Asako and Mr. H. Masuya for their technical assistance, to Mr. H. Kamio and his associates for their physicochemical measurements and Mr. M. Kan and his associates for elemental analysis.

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.

(Received April 19, 1965)

[*4] All melting points are uncorreted.