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Studies on Cyclic vic-Polyketones. I. Syntheses and Characterization of 1,2-Disubstituted Cyclopentenetriones

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Cyclopenten-3,4,5-triones having phenyl, methoxy, and dialkylamino groups at their olefinic double bonds were synthesized, and their structural properties were discussed from their infrared and ultraviolet spectra, and pk values. It is proposed that delocalizability of electron system of the ring is greatly affected by the electron donating ability of the substituent, and that the ring system having strong electron donating groups has a kind of aromaticity.

Compounds with adjacent polyketones, sucn as vicinal triketones (Chart 1) are expected to show unique chemical properties because of their arrangement of functional groups.[2] Among these compounds, squaric acid $C_4H_2O_4$,[3] croconic acid $C_5H_2O_5$[4] and rhodizonic acid $C_6H_2O_6$[5] are the only cases where chemical properties have been investigated.[6] Cyclobutanetetrone, cyclopentanepentone and cyclohexanehexone have been prepared in the hydrated forms. All of their carbonyl groups are hydrated to form gem-diols which resist dehydration.[7] Vicinal polyketones have a large dipole interaction between carbonyl groups and have cross conjugated systems, which are expected to act as a driving force for their chemical reactions.

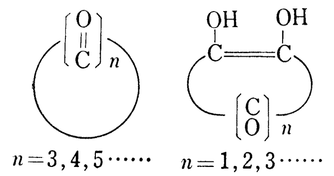

Chart 1

The present paper describes the syntheses and characterizations of several 1,2-disubstituted cyclopentenetriones.

Syntheses

Croconic acid and its esters, triketohydrindene, and other related aromatic condensed analogues are the only cyclopentenetriones having been prepared. As shown in Chart 2, the triketones having aromatic ring and/or amino nitrogen as substituents are prepared. 1-Hydroxy-2-phenylcyclopentene-3,5-dione[8] was oxidized with selenium dioxide in refluxing dioxane to give 1-hydroxy-2-phenylcyclopentene-3,4,5-trione **2a** as red crystals.[9] **2a**(decomp.

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[1] Location: *Hongo 7-3-1, Bunkyo-ku, Tokyo.*

[2] For example, Mc.Caldin, *Chem. Rev.*, **60**, 39 (1960); A. Schönberg and L. Maubasher, *Chem. Res.*, **50**, 261 (1952).

[3] S. Cohen and S. Cohen, *J. Am. Chem. Soc.*, **88**, 1533 (1966); S. Cohen, J.R. Lacher and J.D. Park, *ibid.*, **81**, 3480 (1959); **84**, 2919 (1962).

[4] K. Yamada, Y. Hirata and N. Mizuno, *Bull. Chem. Soc. Japan*, **31**, 543 (1958); K. Yamada and Y. Hirata, *ibid.*, 31., 550 (1958); M. Washino, K. Yamada and Y. Hirata, *ibid.*, **31**, 552 (1958).

[5] R. Nietzki, and T. Benckiser., *Chem. Ber.*, **18**, 1833 (1885) and his related publications.

[6] R. West and H.Y. Niu, *J. Am. Chem. Soc.*, **84**, 1324 (1962); R. West and D.L. Powell, *ibid.*, **85**, 2577 (1963); M. Ito and R. West, *ibid.*, 2580 (1963); R. West and H.Y. Niu, *ibid.*, **85**, 2586 (1963).

[7] F. Bergel, *Chem. Ber.*, **62**, 490 (1919) μ L. philpot, V.J. Graham-Horgan and J. Watson, *Research Supplement*, **6**, 273 (1948); Th. Zincke and A. Ossenbeck, *Lieb. Ann.*, **307**, 1 (1899).

[8] W. Wislicenus and F. Melms, *Lieb. Ann.*, **436**, 101 (1934).

[9] When this compound was isolated from the reaction mixture, it had 1/2 molar equivalent of dioxane as the solvent of crystallization and it showed hydroxyl absorption band near 2500—3000 cm⁻¹. This dioxane was removed from **2a** by heating *in vacuo* to 100—110°.

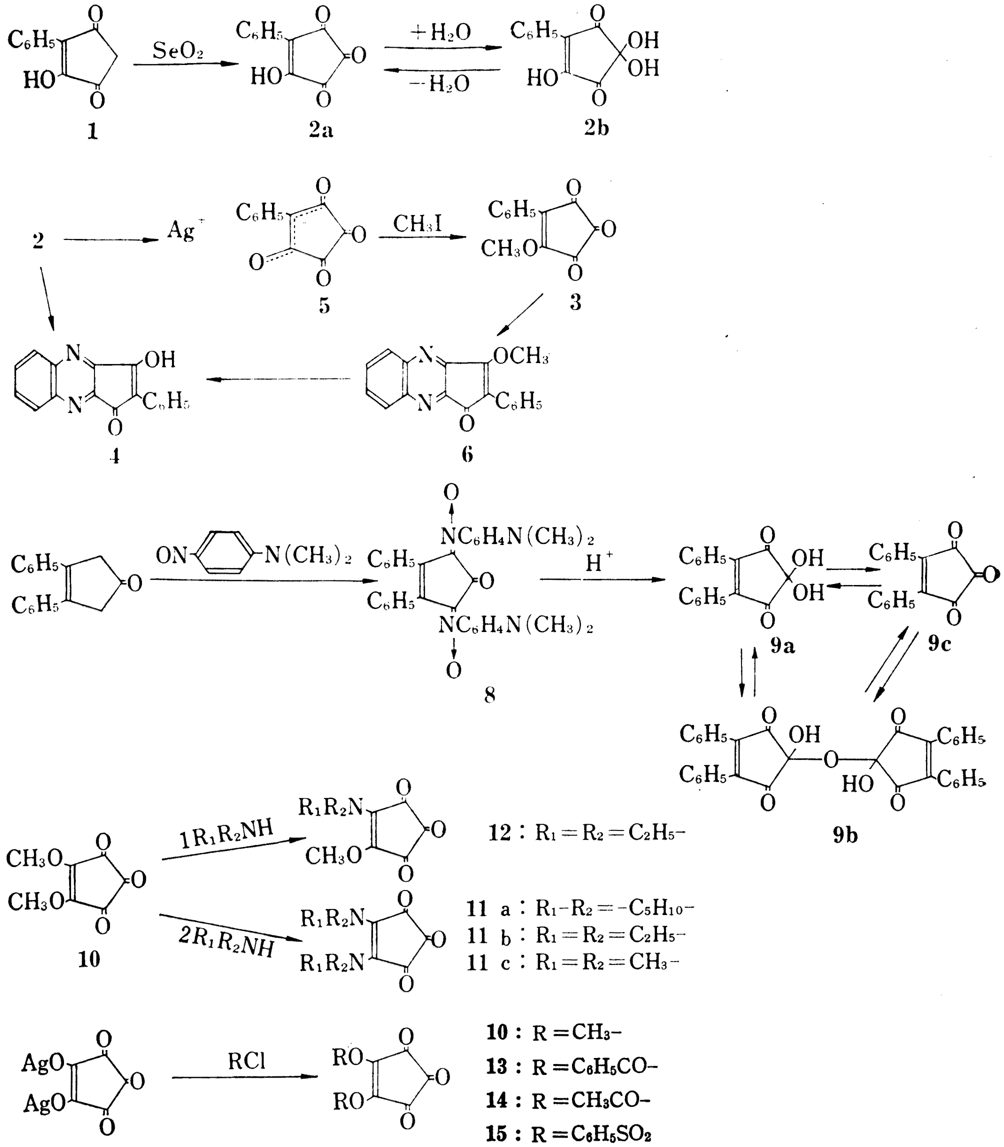

Chart 2

pt 206°) showed in the infrared three carbonyl absorption bands at 1688, 1745 and 1768 cm^{-1}. Treatment of **2a** with aqueous solvent afforded the hydrated triketone **2b** as pale brown crystals (see the experimental part). The water in **2b** is attached to the central carbonyl group to form a gem-diol. This was confirmed by:

1) Pale brown triketone hydrate **2b** shows two carbonyl absorption bands in the infrared (1705 and 1768 cm^{-1}), which is similar to those in pale brown 1,3-diketone **1**.

2) Triketone hydrate **2b** turned to red triketone **2a** by heating *in vacuo* to 60°.

1-Hydroxy-2-phenylcyclopenten-3,4,5-trione **2** formed silver salt with silver nitrate, which was readily converted to methyl ether **3** with methyl iodide. The triketone structure of **2** and **3** was further confirmed by reaction with *o*-phenylenediamine to give quinoxaline derivatives **4** and **6**. Although there are two possible direction in these condensation to form different quinoxaline derivatives, the products obtained were those which was induced from only one direction of condensation and had the structures depicted in the Chart 2. The methyl ether **3** gave a single condensate **6** and acidic hydrolysis of **6** afforded the quinoxaline derivative **4** which was obtained from 1-hydroxy-2-phenyl triketone **2**. The quinoxaline derivative **4** showed carbonyl absorption bands at 1680 and 1570 cm^{-1}. These can be ascribed to the enol group of 1,3-diketone. Nucleophilic attack at more reactive carbonyl group rationalizes product formation.

1,2-Diphenylcyclopenten-4-one[10] was condensed with nitrosodimethylaniline in ethanol to give mainly the dianil-oxide of the triketone **8** as dark purple crystals. This was treated with dilute hydrochloric acid to give 1,2-diphenylcyclopentene-3,4,5-trione hydrate **9a** as yellow crystals. This showed two carbonyl absorption bands at 1750 and 1707 cm^{-1}, and reacted with *o*-phenylenediamine to give a quinoxaline derivative. When **9a** was heated under a reduced pressure, it was dehydrated to give triketone **9c** as a red solid. Compound **9c** showed three carbonyl absorption bands (1772, 1744, and 1694 cm^{-1}). When the hydrate **9a** was recrystallized from benzene, yellow crystals **9b** were obtained, which showed carbonyl absorption bands at 1755, 1735, and 1705 cm^{-1}. These observed IR absorption bands are in a similar region with those of the hydrate **9a**, indicating that there is no central carbonyl group. Its analytical data corresponded to a triketone having 1/2 molar equivalent of water. From these data and consideration of the yellow color of **9b**, the structure of **9b** is proposed as a dimer formed from **9a** and **9c** (this was formed by the dehydration of **9a**) by ketal formation. Compound **9b** could be converted to **9a** or **9c** by treatment with aqueous solvent or heating to 110—120°. Such a type of dimerization in vicinal polyketones was also reported in triketohydrindene.[11]

Dimethyl croconate **10**,[12] was readily reacted with two molar equivalent of aliphatic secondary amines to give 1,2-diaminocyclopentene-3,4,5-triones **11** in good yields. When one molar equivalent of dialkylamine was used, the major product was 1-diethylamino-2-methoxycyclopentenetrione **12**.

Silver croconate was readily converted to 1,2-bis(benzoyloxy)cyclopentene-3,4,5-trione **13** or 1,2-bis(acetoxy)cyclopentene-3,4,5-trione **14** by treatment with benzoyl chloride or acetyl chloride in anhydrous benzene. These compounds **13** and **14** were rather stable in its crystalline state, but was easily hydrolysed in a solution. An attempt to prepare 1,2-bis-(benzenesulfonyloxy)cyclopentene-3,4,5-trione **15** was successful only in an anhydrous condition. This compound was very sensitive to moisture and its structure was verified only by the infrared.

Structural Properties of the Triketones

a) Carbonyl Absoption Bands of the Triketones——Most of the cyclopentenetriones show three absorption bands in the infrared. These are tentatively named as A, B, and C group from the higher ones. These are summerized in Table I.

A is empirically assigned as bands of the central carbonyl groups, because some cyclopentene-3,5-diones do not show bands in this region whereas the other two are present. B and C are assigned as the coupling absorption band of carbonyl groups of the enedione systems. The relative intensity of these groups is generally C>A>B. The region of the observed absorption bands are considerably different in these triketones. For example, the positions of carbonyl absorption of the benzenesulfonyl substituted compound are in a higher frequency region by *ca.* 80 cm^{-1} than those of the amino substituted one. This is very large in comparison to the analogous data for *p*-substituted benzaledehydes (only 23 cm^{-1} from *p*-nitro to *p*-amino compound).

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10) E.J. Corey and H. Uda, *J. Am. Chem. Soc.*, **85**, 1788 (1963).
11) A.R. Lepley and J.P. Thehman, *Tetrahedron*, **22**, 101 (1966); M. Regitz and H-G. Adolph, *Chem. Ber.*, **101**, 3604 (1968).
12) R. Malakovski and S. Prebendovski, *Chem. Ber.*, **71**, 2241 (1938).

Table I. C=O Frequencies of Cyclopententriones

Compds.	R_1	R_2	A	B	C	D	cm^{-1}
11a	$C_5H_{10}N$	$C_5H_{10}N$	1713	1673	1616	1552	(KBr)
11b	$(C_2H_5)_2N$	$(C_2H_5)_2N$	1714 (1727 sh)	1682	1626	1550	(KBr)
12	$(C_2H_5)_2N$	CH_3O	1737	1706	1635	—	(KBr)
10	CH_3O	CH_3O	1761	—	1670	1550	(Nuj)
2a	C_6H_5	HO	1768	1745	1688	1570	(Nuj)
3	C_6H_5	CH_3O	1770	1740	1693	1545	(KBr)
9c	C_6H_5	C_6H_5	1772	1744	1693	1550W	(KBr)
13	C_6H_5COO	C_6H_5COO	1790	1760	1730	1595	(KBr)
14	$C_6H_5SO_3$	$C_6H_5SO_3$	1789	1772	1732	—	(Nuj)

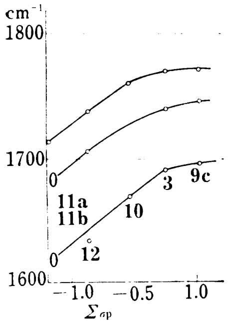


Fig. 1

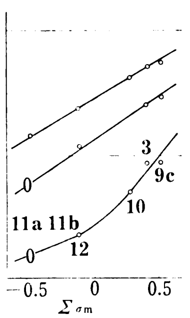


Fig. 2

($\Sigma\sigma_p = \sigma_p$ of $R_1 + \sigma_p$ of R_2, $\Sigma\sigma_m = \sigma_m$ of $R_1 + \sigma_m$ of R_2)

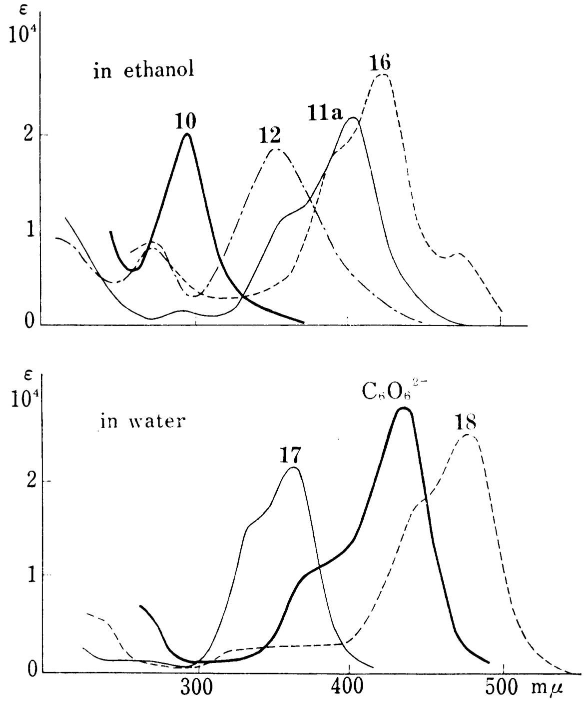


Fig. 3. Ultraviolet and Visible Spectra of Cyclopententriones

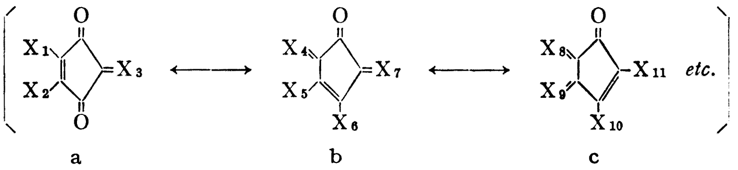
In Fig. 1 and 2, frequencies (cm^{-1}) of the absorption bands are plotted against known σ of the substituents. All three groups exhibit lower frequency shifts with the decrease of σ, indicating that not only are the ketones conjugated with C=C double bonds but also the central ones are strongly affected by the electronic effect of the substituents. It was also observed that, within the limitation of the compounds of which σ of the substituents are known, A and B groups show better linear relationship with σm and C group shows with σp. From these facts, it should be noted that the electron defficiency of the five membered ring caused by the electronic withdrawing effect of the carbonyl groups is strongly supplied by the electron donation from the substituents attached to the olefinic double bond.

The similar nature of these compounds is also observed in the behavior toward water. The hydrated form of the central carbonyl groups of **11** and **12** were not isolated, while those of **2** and **9** were isolated. The qualitative ease of hydrolysis of the C–O and C–N linkage of the substituents was decreasing in the order of **15, 13, 10, 12,** and **11**. 1,2-Bis(benzenesulfonyloxy)-cyclopentene-3,4,5-trione **15**, 1,2-bis(benzoyloxy)cyclopenten-3,4,5-trione **13** and dimethyl croconate **10** were very easily hydrolyzed. 1-Diethylamino-2-methoxycyclopentenetrione **12** was gradually hydrolyzed in water at its enol ether linkage (completely in 26° for 75 minutes) and formed 1-hydroxy-2-diethylamino cyclopentenetrione **18** from the ultraviolet analysis.

Diaminotriketones **11a**—**c** showed no tendency to be hydrolyzed by keeping them in water for 2 days from the ultraviolet analysis.

b) Ultraviolet Spectra of the Triketones——Ultraviolet and visible spectra of the several triketones which are stable in the condition of measurement are shown in Fig. 3.

The absorption spectra of **10**—**12** showed marked red shift with increase of the electron donating effect of the substituents. The shapes of the absorption bands resemble that of the resonance stablized croconate ion **17** as the absorption maxima of these compounds shift. This tendency is more pronounced in the case of 1,3-dipiperidylcyclopentene-2,4,5-trione **16**.[13] It is reasonable to assume that an increase of the electron donating ability of the substituents lower the π-electron energy by electron delocalization. This is also explicable if we conveniently assume the ratio of the contribution of classical resonance structures as shown in Chart 3.



17: $X_1=X_2=X_5=X_6=X_{10}=X_{11}=O^-$, $X_3=X_4=X_7=X_8=X_9=O$

10—12: $X_1=X_2=X_5=$O-alkyl or N-(alkyl)$_2$,
$X_4=X_8=X_9=O^+$-alkyl or N$^+$-(alkyl)$_2$,
$X_3=X_7=O$, $X_6=X_{10}=X_{11}=O^-$

13—15,18: $X_1=$N-(alkyl)$_2$, $X_4=X_8=$N$^+$-(alkyl)$_2$,
$X_2=X_5=X_6=X_{10}=X_{11}=O^-$, $X_3=X_7=X_9=O$

16: $X_1=X_{11}=$N-(alkyl)$_2$, $X_3=X_4=X_7=X_8=$N$^+$-(alkyl)$_2$,
$X_2=X_5=X_6=X_{10}=O^-$, $X_3=X_9=O$

Chart 3

In croconate ion **17**, the extent of contribution of (a), (b) and (c) are equal. But the extents of contribution of (b) and (c) in **10**—**15** and **18**, and of (b) in **16** are not equal to those of (a). Their extents depend on how much electron donating ability their substituents have.

The Acidity Constants of the Polyketoenols

Strong acidity constants of croconic acid and squaric acid are considered to be due to large DE/π of their anions. pK of 1-Hydroxy-2-phenylcyclopententrione **2** which is a member of the aromatic oxocarbon anions proposed by R. West,[6] was measured by potentiometic titration, showing 1.75 (in water) and 2.46 (in 50% ethanol). This result shows that, as R. West has predicted, **2** is a very strong acid for a compound having an enolic hydroxyl group and that its acidity is comparable to those of its homologues: 2-hydroxy-1-phenylcyclopropenon (pK 2.2) and 2-hydroxy-1-phenylcyclobutenedione (pK 0.37—0.04). From the result of LCAO MO calculation on these three compounds,[6] DE/π is the largest in the three membered ring and the least in the five membered one. However, the relative acidities of these three are not parallel to the calculated DE/π. The pK of several polyketoenols including those of which were newly measured in this research are listed in Table II.

The dissociation constant of 1,2-dihydroxy-3,5-dione **19**[13] (pK_1=4.55 in 50% ethanol) is only 10% of 1-hydroxy-2-phenyl-3,5-dione **1** (pK_1=3.55 in 50% ethanol), while the dissociation constant of 1,2-dihydroxy trion **17** (croconic acid, pK_1=0.3—0.7 in water) is 100 times as that of 1-hydroxy-2-phenyltrione **2** (pK_1=1.75 in water). In the 1-hydroxy-2-phenyl system, the dissociation constant is increased only by a factor of 80 by change of compound

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[13] The preparation of this compound is to be published in the forthcoming paper.

Table II. Acidity of Cyclic Polyketoenols

Compounds	pK	references
1-Phenyl-2-hydroxycyclopentene-3,5-dione **1**	3.55 (tit. in 50% EtOH)	
1-Phenyl-2-hydroxycyclopentene-3,4,5-trione **2**	1.75 (tit. in H_2O) 2.46 (tit. in 50% EtOH)	
1,2-Dihydroxy-4,4-di-*p*-tolylcyclopentene-3,5-dione	$k_1=4.55$ $k_2=9.82$ (tit.in 50% EtOH)	
1-Phenyl-2-hydroxycyclopropenone	2.0 0.5 (spectr) 2.2 (tit.)	D.G. Farnum, D.E. Thurston, *J. Am. Chem. Soc.*, **88**, 3075 (1966)
1-Phenyl-2-hydroxycyclobutenedione	0.37 0.04	E.J. Smutny, J.D. Robert, *J. Am. Chem. Soc.*, **82**, 1793 (1962)
Squaric acid	$k_1=2.10^{-3}$	D.T. Ireland, H.F. Walton, *J. Phys. Chem.*, **71**, 751 (1967)
Croconic acid	$k_1=0.3$—0.5 $k_2=1.4$—1.6 (tit.)	B. Carlquist, *Acta Chim. Scand.*, **16**, 94 (1962)
	$k_1=0.68$ $k_2=1.97$ (spectr)	P. Souchay, M. Fleury, *Compt. Rend.*, **252**, 737 (1961).
Rhodizonic acid	$k_1=3.37$ $k_2=4.7$ (tit.)	G. Carpeni, *J. Chim. Phys.*, **35**, 193 (1938)
	$k_1=4.1$ $k_2=4.5$	P.W. Preisler, L. Berger, *J. Am. Chem. Soc.*, **69**, 326 (1947)

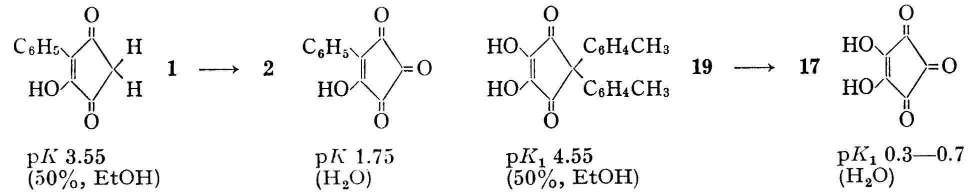

Chart 4

from the diketone to the triketone, while, in the 1,2-dihydroxy system this increase is 10^4 for the same change

There are two main factors in the contribution of the central carbonyl group to stabilize the triketoenol anions. One is the inductive effect and the other is the conjugation effect to π system. As the former should be equal in the above two systems, the difference in the increase of dissociation in these two system should be attributable to the difference in the ratio of conjugation of the central carbonyl groups to the polyketoenol anion systems. Because the hydroxyl group is a stronger electron donor through system than the phenyl group, it can more stablize the polyketoenol anion.

The difference in stability of these two anions is also observed in the behavior of these compounds in alkali. Croconic acid **17** is stable to caustic alkali, but, **2** is gradually decomposed even in aqueous solution from pH 9. This degradation process has not been investigated.

From the properties of the cyclopententriones observed in the infrared, ultraviolet spectral measurement and acidity constants described above, it is shown that this ring system has a strong tendency for supplying electrons from substituents attached to the olefinic double bond, and consequently, it is supposed that this ring system contains a fair amount of delocalization energy. R. West, *et al.* reported that cyclic vicinal polyketone anions have large delocalization energy per *pi*, and has named them new aromatic oxocarbon anions. But, new aromatic in the above meaning should not only be restricted to such anionic compounds. Such compounds are the cyclic polyketones which are stablized by being supplied electrons from outside of molecules. Cyclopentenetriones which are fairly supplied with electrons from their own substituents have the stability in the similar way.

Experimental

1-Hydroxy-2-phenylcyclopentene-3,4,5-trione (**2**)——To a solution of SeO_2 (6 g, 54 mmole) in warm dioxane (150 ml), 1-phenyl-2-hydroxycyclopentene-3,5-dione **1** (10 g, 53 mmole) was added. The mixture was refluxed for 6 hr with stirring. After cooling, deposited Se were filtered off (4.0 g, 93%) and the filtrate was condensed under reduced pressure. The precipitated red crystals were collected (5.5 g) and were recrystallized from benzene–dioxane. mp 206° (dp) *Anal.* Calcd. for $C_{11}H_6O_4 \cdot 1/2C_4H_8O_2$: C, 63.41; H, 4.09. Found: C, 63.66; H, 4.22. UV λ_{max} (ethanol) mμ (log ε): 242 (4.00), 323 (4.11), 435 (3.89). IR (KBr, cm^{-1}): 1688, 1745, 1768 ($\nu_{C=O}$). Recrystallization of **2a** from aqueous dioxane for five times afforded the hydrated triketone as pale brown crystals. *Anal.* Calcd. for $C_{11}H_6O_4 \cdot 2H_2O$: C, 55.46; H, 4.23. Found: C, 56.05; H, 4.28. IR (KBr, cm^{-1}): 1705, 1768 ($\nu_{C=O}$). The water of crystallization was removed under reduced pressure (10^{-2} mmHg) at room temperature afforded **2b**. *Anal.* Calcd. for $C_{11}H_6O_4 \cdot H_2O$: C, 60.00; H, 3.66. Found: C, 59.61; H, 3.66.

The hydrated water was removed from **2b** under reduced pressure (10^{-2} mmHg) at 60° to give anhydrous triketone. *Anal.* Calcd. for $C_{11}H_6O_4$: C, 65.34; H, 2.99. Found: C, 65.08; H, 3.14. IR (KBr, cm^{-1}): 1688, 1745, 1768 ($\nu_{C=O}$).

1-Methoxy-2-phenylcyclopentene-3,4,5-trione (**3**)——To a solution of 1-hydroxy-2-phenylcyclopentenetrione **2** (1.2 g) in water, an excess of a saturated solution of silver nitrate in water was added, and the precipitated red salt **5** was collected and washed with water 1.4 g. After this was dried *in vacuo*, this salt was suspended in 100 ml of anhydrous ether and 3.2 g of methyl iodide was added. The mixture was stirred for one night and the silver salts were filtered and washed with anhydrous ether. The ether layers were combined, and the solvent was evaporated under a reduced pressure to give 0.32 g (33%) of 1-methoxy-2-phenylcyclopentene-3,4,5-trione **3** as a red mass. UV λ_{max} (ethanol) mμ (log ε): 240 (3.88), 319 (3.97), 435 (3.33). IR (KBr cm^{-1}): 1690, 1738, 1769 ($\nu_{C=O}$). NMR ($CDCl_3$) τ: 5.33 (3H, s), 1.85 and 2.50 (5H, m). *Anal.* Calcd. for $C_{12}H_8O_4$: C, 66.67; H, 3.73. Found: C, 66.53; H, 3.91.

Condensation of 1,2-Diphenylcyclopentene-4-one (**7**) **with *p*-Nitrosodimethylaniline**——A mixture of 1,2-diphenylcyclopentene-4-one (4.8 g, 20.6 mmol), *p*-nitrosodimethylaniline (12.5 g, 83.5 mmol) and 0.03 ml of concentrated hydrochloric acid in 150 ml of anhydrous ethanol was boiled under reflux for 2 hours. After the reaction mixture had stood in a refrigerator for one night, the precipitated dark brown crystalline mass was collected, washed with large amount of ethanol to give the condensate **8** (3.74 g, 34.4%). *Anal.* Calcd. for $C_{33}H_{30}O_3N_4$: C, 74.69; H, 5.70; N, 10.56. Found: C, 75.38; H, 5.78; N, 10.86. The purification of the condensate **8** by recrystallization was unsuccessful.

Hydrolysis of the Condensate (**8**) **with Dilute Hydrochloric Acid**——3.5 g of the condensate **8** was suspended in a mixture of ether (100 ml) and water (100 ml), and concentrated hydrochloric acid (30 ml) was added dropwise within 30 min. The reaction mixture was allowed to stirr for an additional 30 min. The orange colored ether layer was separated, and the water layer was washed with ether several times. The ether layers were combined, washed with small amount of water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residual oily mass was chromatographed over silica gel to give 1.1 g of 1,2-diphenylcyclopentene-3,4,5-trione monohydrate **9a**. mp 131—132°. *Anal.* Calcd. for $C_{17}H_{10}O_3 \cdot H_2O$: C, 72.85; H, 4.32. Found: C, 73.09; H, 4.30. **9a** was recrystallized from benzene to give **9b** as yellow prisms. mp 142—143.5°. *Anal.* Calcd. for $C_{17}H_{10}O_3 \cdot 1/2\,H_2O$: C, 75.27; H, 4.23. Found: C, 75.45; H, 4.30. A methanolic solution of **9b** had stood at room temperature and the solvent was evaporated to yield the hydrate **9a** as an yellow mass. Both **9a** and **9b** were warmed *in vacuo* to 110—120° for 4 hours, these compounds turned to red anhydrous **9c**. This was a red mass and was readily converted to **9a** by standing in the air for one night.

Dimethyl Croconate (**10**) (**A Modified Method of Ref. 12**)——Disilver croconate (38 g, dried at 50—60° for several hours *in vacuo*) was placed in a Soxhlet extracter, which was fitted on a flask containing methyl iodide (30 g) and anhydrous benzene (300 ml). This was heated under reflux for 2 hours. The orange reaction solution was concentrated to 40 ml and cooled. The precipitated orange yellow crystals were collected and washed with a small amount of anhydrous benzene to give dimethyl croconate (14 g, 73%). mp 114—117° (114—115°,[2] 113—114°[4]). This compound is unstable to water and should be kept from atmospheric moisture.

Reaction of Dimethyl Croconate (**10**) **with Secondary Aliphatic Amines**——a) To a solution of dimethyl croconate (1.86 g, 10.4 mmole) in anhydrous benzene and tetrahydrofuran, piperidine (4.5 g, 53 mmole) was added. The solution was stirred at room temperature for 4 hours. The precipitated orange red crystals were collected and washed with benzene to give substantially pure 1,2-dipiperidylcyclopentene-3,4,5-trione **11a** (2.73 g, 90%). mp 198—199°. UV λ_{max} (ethanol) mμ (log ε): 488 (3.92), 414 (4.43), 370—385 (sh) (1.25). NMR ($CDCl_3$) τ: 8.24 (12H, m), 6.18 (8H, m). IR (KBr, cm^{-1}): (1727 sh), 1716, 1674, 1615 ($\nu_{C=O}$). *Anal.* Calcd. for $C_{15}H_{20}O_3N_2$: C, 65.19; H, 7.30; N, 10.14. Found: C, 65.42; H, 7.12; N, 10.32.

b) Dimethyl croconate (**10**, 1.7 g, 10 mmole) and diethylamine (2.0 g, 27.4 mmole) were reacted in similar way as (a). After evaporation of the solvent, the residual solid was chromatographed on silica gel. Elution with methylene chloride gave 1,2-bis(diethylamino)cyclopentene-3,4,5-trione **11b** (1.44 g). Recrystallization from carbon tetrachloride gave 0.98 g of pure **11b** as red crystals. mp 117—118°. UV λ_{max} (ethanol) mμ (log ε): 375 (sh), 405 (4.26), 510 (3.66). NMR ($CDCl_3$) τ: 8.83 (12H, t), 6.38 (8H, q). IR (KBr) cm^{-1}: 1714, 1682, 1626 (ν c=o). *Anal.* Calcd. for $C_{13}H_{20}O_3N_2$: C, 61.90; H, 7.94; N, 11.11. Found: C, 62.17; H, 8.18; N, 11.09.

c) Dimethyl croconate (**10**, 1.7 g, 10 mmole) and dimethylamine (1.35 g, 30 mmole) were reacted in similar way to give 1,2-bis(dimethylamino)cyclopentene-3,4,5-trione **11c** (1.85 g, 97%). Recrystallization from chloroform gave 1.6 g of the pure **11c**. mp 213—215°. UV λ_{max} (ethanol) mμ (log ε): 370 (4.05) 401 (4.11), 530 (3.41). NMR ($CDCl_3$) τ: 6.68 (12H, s). IR (KBr) cm^{-1}: 1701, 1655, 1608 (ν c=o). *Anal.* Calcd. for $C_9H_{12}O_3N_2$: C, 55.09; H, 6.12; N, 14.28. Found: C, 54.85; H, 5.98; N, 14.26.

d) Dimethyl croconate (3.64 g, 21.4 mmole) and 2.0 g (27.4 mmole) of diethylamine were similarly reacted. After evaporation of the solvent, the residual mass was chromatographed on silica gel with benzene–chloroform as an eluent to yield 1-diethylamino-2-methoxycyclopentene-3,4,5-trione **12** as orange crystals (2.91 g, 64.4%) and 1,2-(diethylamino)cyclopentene-3,4,5-trione **11b** (0.39 g, 5.4%). Properties of **12**, mp 87—89° (from carbon tetrachloride). UV λ_{max} (ethanol) mμ (log ε): 270 (3.88), 3.54 (4.28). NMR ($CDCl_3$) τ: 8.67 (6H, t), 6.13 (4H, m), 5.44 (3H, s). IR (KBr) cm^{-1}: 1737, 1706, 1635 (ν c=o). *Anal.* Calcd. for $C_{10}H_{13}O_4N$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.60; H, 6.34; N, 6.93.

1,2-Bis(benzoyloxy)cyclopentene-3,4,5-trione (**13**)——Disilver croconate (1 g, dried at 50—60° for several hours *in vacuo*) and benzoylchloride (excess) were reacted in similar way to give 1,2-bis(benzoyloxy)-cyclopentene-3,4,5-trione **13** (0.9 g, 92%). Recrystallization from dry benzene gave 0.6 g of pure **13**, as orange crystals. mp 158—160°. IR (KBr) cm^{-1}: 1790, 1760, 1730 (ν c=o). *Anal.* Calcd. for $C_{19}H_{10}O_7$: H, 2.86. Found: C, 64.98; H, 3.00.

1,2-Bis(acetoxy)cyclopentene-3,4,5-trione (**14**)——1,2-Bis(acetoxy)cyclopentene-3,4,5-trione was synthesized from disilver croconate and acetylchloride in a similar way as above. mp 137—140°.

Reaction of the Triketones with *o*-Phenylenediamine——a) A solution of a triketone and excess of *o*-phenylenediamine in ethanol was boiled under reflux for several hours. After cooling, the precipitated crystalline product was collected and recrystallized from ethanol-methylene chloride.

b) A mixture of a triketone and 0.5—1 molar equivalent of *o*-phenylenediamine in methanol was stirred at a room temperature for half an hour. The precipitated crystalline product was collected and washed with methanol or recrystallized from methanol. The result of elemental analyses and melting points of the quinoxaline derivatives of the cyclopentenetriones are as follow (R_1 and R_2 are the substituents in the triketones).

Triketone	R_1	R_2	mp	Formula	Anal. % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Method
11a	$C_5H_{10}N$	$C_5H_{10}N$	198.5—199.5°	$C_{21}H_{24}ON_4$	72.38	6.94	16.08	72.57	6.98	15.93	(a)
9	C_6H_5	C_6H_5	228.5—229.5°	$C_{23}HL_4ON_2$	82.61	4.22	8.38	82.46	4.00	8.11	(a)
2	OH	C_6H_5	264 —265°	$C_{17}H_{10}O_2N_2$	74.44	3.68	10.21	74.15	3.74	10.07	(b)
3	OCH_3	C_6H_5	192 —193.5°	$C_{18}H_{12}O_2N_2$	74.99	4.20	9.72	75.16	4.22	9.82	(b)

Hydrolysis of 1-Methoxy-2-phenyl-1H-cyclopenta[*b*]quinoxalineone (**6**)——A suspension of the condensate **6** (83 mg) in methanol (5 ml), water (2 ml) and concentrated hydrochloric acid (2 ml) was warmed to 70° for 30 min. After the reaction mixture was allowed to come to room temperature, the dark brown crystals were collected and washed with methanol to afford 74 mg of **4**.

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