Stable Enols of Carboxylic Esters. The Poly(methoxycarbonyl)cyclopentadiene Systems

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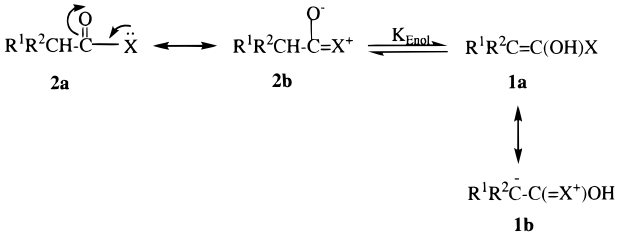
Received January 12, 2000

The structures of the poly(methoxycarbonyl)cyclopentadienes $C_5H_{6-n}(CO_2Me)_n$, $n = 5$ (**Cp-5**), $n = 4$ (**Cp-4**), $n = 3$ (1,2,4-; **Cp-3**) and $n = 2$ (1,2-; **1,2-Cp-2-I**) were investigated. The X-ray diffractions of **Cp-5** (known), **Cp-4**, and **Cp-3** showed an enol of ester structure in the solid state. The enolic hydrogen forms a symmetrical hydrogen bond to a neighboring ester carbonyl, so that the vicinal "enolic" CO_2Me groups in the 1,2-C(=CO_2Me)−C(CO_2Me)$_4$ moiety are identical. The relevant X-ray parameters for the three enols are similar. The CP-MAS spectra of **Cp-3**−**Cp-5** generally resemble their ^{13}C NMR spectra in $CDCl_3$ except for some differences of mostly <1 ppm. The ^1H, ^{13}C, and ^{17}O NMR spectra of **Cp-3**−**Cp-5** in $CDCl_3$ are consistent with those of the hydrogen bonded enols. Most characteristic are the ^1H and ^{17}O signals of the OH groups at 19.7−20.1 and 221−225 ppm, respectively. Proton addition to sodium 1,2-bis(methoxycarbonyl)cyclopentadienide gave a mixture of four 1,2-bis(methoxycarbonyl)cyclopentadienes. The isomer (**1,2-Cp-2-I**) formed in 10−20% displays $\delta(O^1H)$ at 19.3 ppm and is the enol analogue of **Cp-5** whereas its main isomer (30−55%) (**1,2-Cp-2-IV**) has the ester structure. In CD_3CN and DMSO-d_6 only one signal was observed at room temperature for each type of H, C, or O of **Cp-5**, suggesting a complete ionization to the symmetrical anion of **Cp-5**. In contrast, **Cp-4** and **Cp-3** in CD_3CN at room temperature display OH signals in both ^1H and ^{17}O NMR spectra, and **Cp-5** shows a broad OH signal in the ^1H spectrum at 240 K. The enol of ester structure is the main species, although exchange with the corresponding anion is possible. On standing in DMF-d_7 at room temperature, new signals are observed for **Cp-3** and **Cp-4**. On raising the temperature in $Cl_2CDCDCl_2$, **Cp-3**−**Cp-5** show line broadening and appearance of new signals. These were ascribed to rearrangment and decomposition processes.

Introduction

Observable enols of carboxylic acid derivatives **1** (= **1a**/**1b**), X = OH, OR′, halogen, NR′R″, OCOR′ are rare species.[1] The main reason given for this is a mesomeric electron donation by the group X which increases the stability of the carboxylic acid species **2a** (cf. hybrid **2b**), thus making the enol relatively unstable (cf. eq 1).[1a] This



(1)

instability was evaluated computationally for various systems by various methods.[2,3] For example, for the pair methyl acetate/1-methoxyethenol, the calculated energy difference in favor of the ester form is ca. 30 kcal/mol at various levels of calculations.[3] Calculations also indicated two ways of reducing this gap. A substantial reduction which still leaves an extensive gap is by substituting the system by β-bulky aryl substituents.[4] A more efficient way is by introducing β-electron-withdrawing groups (EWGs) which have a multifold effect. (i) They increase the importance of hybrid **1b** of the enol by delocalizing its negative charge on C_β. (ii) Frequently they can form a hydrogen bond with the enolic OH group. (iii) A repulsion between their dipoles and the dipole of the CO group in **2a** raise the energy of the acid derivative form. When these effects are important, the enol derivative **1** may become relatively more stable than its isomeric acid derivative **2**. Several enols of carboxamides carrying strongly β-EWGs are known,[5] and others were recently prepared.[6]

Enols of esters are rarely observed or detected compared with enols of amides. They belong to three groups. (i) Derivatives of alkyl β,β-(di-bulky aryl) acetates **3a**−**c**

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10.1021/jo000046a CCC: $19.00
Published on Web 05/26/2000

were observed as short-lived intermediates,[7a−c] and (ii) malonic ester derivatives were detected by classical enol identification methods.[7d] (iii) Two solid-state structures of compounds substituted with EWGs, i.e., a Meldrum's acid derivative[8] and pentakis(methoxycarbonyl)cyclopentadiene **Cp-5**[9] are the only enols of esters found in the Cambridge Structural Database (CSD).

$$Ar_2C{=}C(OH)OR$$

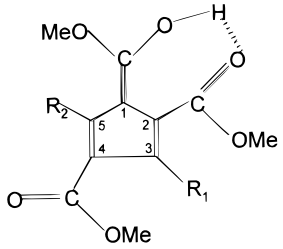
3 **a**: Ar = Me_5C_6, R = *t*-Bu

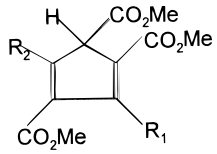
b: Ar = 2,4,6-*i*-$Pr_3C_6H_2$, R = Me

c: Ar = 2,4,6-$Me_3C_6H_2$, R = Me

Cyclopentadiene derivatives are strong potential candidates for the R^2R^1C-moiety in observable and long-lived enols **1**. First, cyclopentadiene is capable of delocalizing a negative charge, and this ability increases on substitution by EWGs. Moreover, more than two EWGs can be attached to a cyclopentadiene, and their number increases in derivatives such as indene and fluorene. Second, a substantial part of enols **1**, X = OH studied by Kresge and Wirz are *β*-cyclopentadienylidene, *β*-indenylidene, and *β*-fluorenylidene derivatives[10] and comparison of their acid/enol equilibrium constants with those of substituted systems is possible. Third, the ester **Cp-5** is enolic in the solid state.[9] However, we note the report that an enolic ^{1}H signal was not observed for 1,2,3,4-tetrakis(methoxycarbonyl)cyclopentadiene.[11]

Consequently, we prepared and studied the structures of the poly(methoxycarbonyl)cyclopentadienes $C_5H_n(CO_2Me)_{6-n}$, $n = 1$ (**Cp-5**), $= 2$ (**Cp-4**), and $= 3$ (the 1,2,4-derivative, **Cp-3**) in both the solid state and in solution. As shown below they mostly exist in the hydrogen bonded enolic structure written, rather as the "ester" forms **4a**−**c**. The mixture of the 1,2- and 1,3-isomers (i.e., $n = 4$) was also investigated in solution.





Cp-3	$R_1 = R_2 = H$	**4a**	$R_1 = R_2 = H$
Cp-4	$R_1 = CO_2Me$, $R_2 = H$	**4b**	$R_1 = CO_2Me$, $R_2 = H$
Cp-5	$R_1 = R_2 = CO_2Me$	**4c**	$R_1 = R_2 = CO_2Me$

Results and Discussion

Synthesis. 1,2,3,4,5-Pentakis(methoxycarbonyl)cyclopentadiene (**Cp-5**) was prepared according to Bruce et al.[9b] Its partial hydrolysis/decarboxylation with KOH gave the potassium salt of **Cp-4**, which on protonation gave 1,2,3,4-tetrakis(methoxycarbonyl)cyclopentadiene (**Cp-4**). Under somewhat similar conditions hydrolytic decarboxylation of **Cp-5** gave 1,2,4-tris(methoxycarbonyl)cyclopentadiene (**Cp-3**). Attempts to generate pure 1,2-bis(methoxycarbonyl)cyclopentadiene (**Cp-2**) from its salts gave mixture of either the sodium salts of **Cp-2** and its 1,3-isomer or of the salts of **Cp-2** and **Cp-3**. On protonation of a 93:7 mixture of the salts of the 1,2- to the 1,3-diester, the ^{1}H NMR spectrum obtained was very close to that of pure **Cp-2**. Note that in a previous work[12] a 1,2- and 1,3-diesters mixture was studied due to difficulty in their separation.

Potassium 1,2,3-tris(methoxycarbonyl)cyclopentadiene which was obtained in a mixture with its 1,2,4-isomer[13] was not protonated to the pure acid. Its rhodicinium salt was obtained from a reaction of **Cp-5**.[14] We failed to

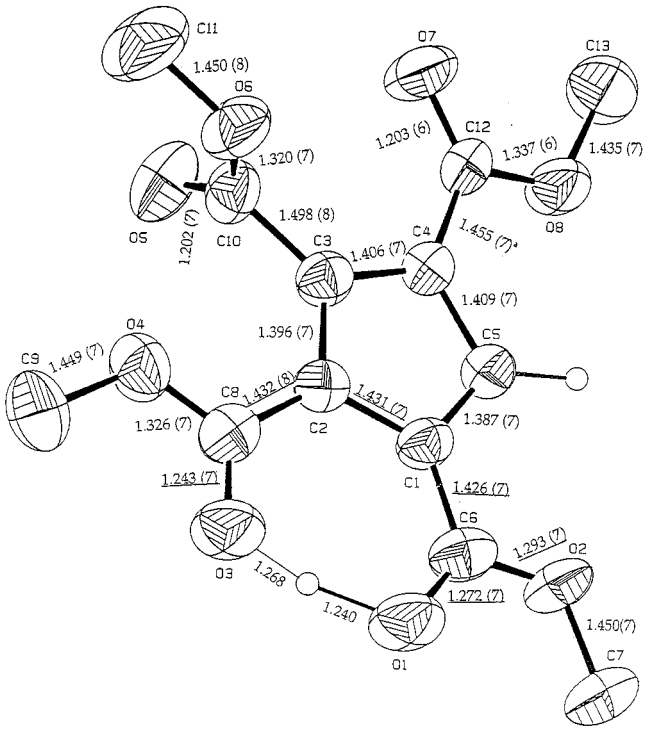


Figure 1. An ORTEP drawing of **Cp-4**.

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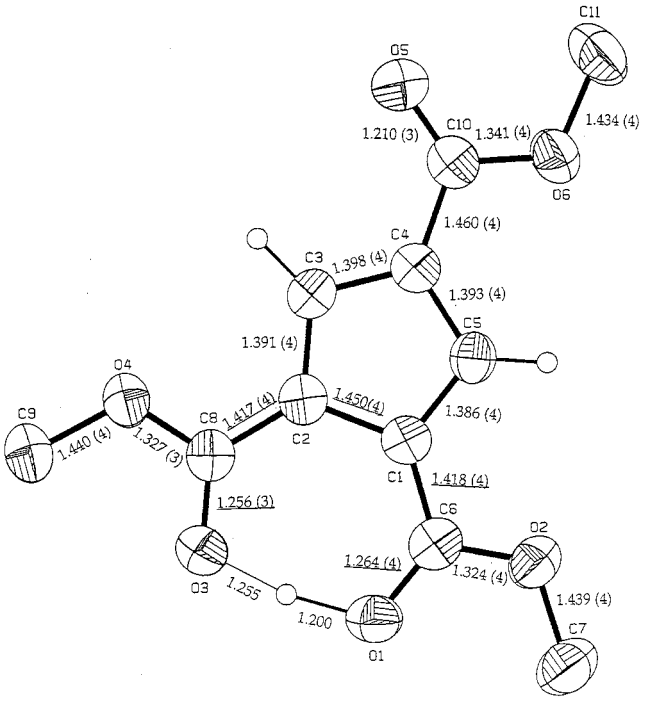

Figure 2. An ORTEP drawing of **Cp-3**.

obtain 1,2,3-tris(methoxycarbonyl)cyclopentadiene by a method analogous to those described above.

Solid State Structure of Cp-5, Cp-4, and Cp-3. The published[9] X-ray structure of **Cp-5** is that of an enol of ester, where the carbonyl group of the C2-CO_2Me ester group forms a short and strong intramolecular hydrogen bond with the enolic hydrogen.[15] Characteristic features are O(1)−H and O(3)···H bond lengths of 1.12 (4) and 1.32 (4) Å, an elongated C1−C2 bond of 1.453 (5) Å, relatively short C(ring)−C(CO_2Me) bonds, and long C−O bonds of the former carbonyls of the enol moiety.[9]

We obtained X-ray diffraction data of both **Cp-4** and **Cp-3**. Their ORTEP drawings with superimposed bond lengths are given in Figures 1 and 2. Crystallographic data, bond lengths, bond angles, and thermal and positional data are given in Tables S1−S10, and stereoviews are in Figures S1 and S2 of the Supporting Information.

Comparative data for **Cp-5, Cp-4**, and **Cp-3** are given in Table 1. The literature[9] atom numbering of **Cp-5** was adjusted to that of **Cp-4** in order to facilitate the comparison. Bond lengths relevant to the enolic moiety are underlined. The following features are relevant for both the structure assignment and the comparison of the three substrates. (a) The three compounds have very similar structures, disregarding differences due to the different number of CO_2Me groups. Most important is the presence of the cyclic seven atom C1C2C8HO3O1C6 enol of ester moiety, having an enolic O−H group hydrogen bonded to a neighboring carbonyl. This moiety is symmetrical or nearly so, i.e., it is practically impossible to distinguish between the two former CO_2Me groups, the enolic one and its hydrogen bonding acceptor neighbor. Accordingly, the ring carbon−*C*(O_2Me) carbon bonds are significantly shorter, being 1.427 ± 0.001 Å, 1.429 ± 0.003 Å, and 1.418 ± 0.001 Å for **Cp-5**, **Cp-4**, and **Cp-3**, respectively, compared with 1.455−1.498 Å for the corresponding bonds of the other "normal" CO_2Me groups in our systems[15] and to the average value of 1.496 Å from the CSD.[16] Hence, the double bond character of the exocyclic C=C bonds in the enols is evident. The C−O bonds of this moiety are 1.243−1.272 Å, i.e., significantly longer than 1.194−1.210 Å for the "nonenolic" normal C=O bonds of other ester carbonyls[15] and the CSD value of 1.196 Å.[16] (b) The hydrogen bonds are symmetrical within the experimental error of O−H bond lengths. The largest difference Δ(OH) between the two bond lengths is of 0.2 Å for **Cp-5**,[9] whereas the values are 0.028 Å for **Cp-4** and 0.055 Å for **Cp-3**. These bonds are not far from linearity: the O1−H−O3 angle being 150° for **Cp-4** and 166.9° for **Cp-3**, and the O1−O3 distances are 2.42 Å for **Cp-4** and 2.44 Å for **Cp-3**. Thus, the hydrogen bonds are

Table 1. Bond Lengths (Å) in Cp-3−Cp-5

bond	Cp-3[a]	Cp-4[b]	Cp-5[c]
C(ring)−C(ring)			
C(1)−C(2)	1.450(4)	1.431 (7)	1.453 (5)
C(2)−C(3)	1.391 (4)	1.396 (7)	1.396 (3)
C(3)−C(4)	1.398 (4)	1.406 (7)	1.410 (5)
C(4)−C(5)	1.393 (4)	1.409 (7)	1.408 (4)
C(1)−C(5)	1.386 (4)	1.387 (7)	1.403 (4)
C(ring)−C(ester)			
C(1)−C(6)	1.418 (4)	1.426 (7)	1.426 (4)
C(2)−C(8)	1.417 (4)	1.432 (8)	1.428 (5)
C(4)−C(10)	1.460 (4)	1.455 (7)[d]	1.460(3)
C(3)−C(10)		1.498 (8)	1.497 (5)
C(5)- C((12)			1.488 (5)
ester C=O			
C(6)−O(1)	1.264 (4)	1.272 (7)	1.259 (4)
C(8)−O(3)	1.256 (3)	1.243 (7)	1.256 (3)
C(10)−O(5)	1.210 (3)	1.202 (7)	1.194 (4)
C(12)−O(7)		1.203 (6)	1.198 (4)
C(14)−O(9)[c]			1.205 (4)
ester C−O			
C(6)−O(2)	1.324 (4)	1.293 (7)	1.320 (5)
C(8)−O(4)	1.327 (3)	1.326 (7)	1.316 (4)
C(10)−O(6)	1.341 (4)	1.320 (7)	1.342 (4)
C(12)−O(8)		1.337 (6)	1.331 (4)
C(14)−O(10)[c]			1.328 (4)
ester O−Me			
O(2)−C(7)	1.439 (4)	1.450 (7)	1.472 (5)
O(4)−C(9)	1.440 (4)	1.449 (7)	1.460 (5)
O(6)−C(11)	1.434 (4)	1.450 (8)	1.455 (6)
O(8)−C(13)		1.435 (7)	1.443 (4)
O(10)−C(15)			1.452 (8)
hydrogen bond			
O(1)−H	1.200	1.240	1.12 (4)
O(3)−H	1.255	1.268	1.32 (*4*)

[a] For atom numbering, see Figure 2. [b] For atom numbering, see Figure 1. [c] From ref 9; atom numbering was adjusted to that of Figure 1. The C(5)-ester group is C(14)(=O9)O(10)C(15)H_3. [d] C(4)−C(12).

Table 2. ^{13}C−CP-MAS Data (δ in ppm) for the Solid Esters Cp-3−Cp-5

Cp-3	Cp-4	Cp-5	Cp-3	Cp-4	Cp-5
50.0	50.5	49.6	128.9	134.0	126.3
51.4	51.7	51.9			127.6[a]
54.7	54.9	53.4			133.7[a]
	58.6	56.0			134.9[a]
110.0	107.6	104.9	163.4	163.7	166.9
113.4	118.3	112.0	168.7	168.3	168.7
121.5	123.5[a]	114.1	171.9	171.4	171.7
127.5	128.4	117.5		173.1	

[a] Low intensity signals.

(15) Whereas the numbering of the carbons in the acid forms **4** should start with the vinylic carbon, and hence C5 is the sp^3-hybridized carbon, we number this sp^2-hybridized carbon as C1 in all the enols.

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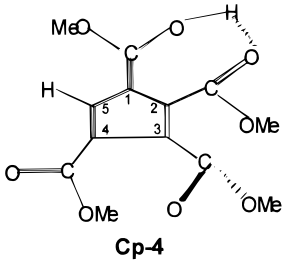
Table 3. NMR Spectra (δ in ppm) at 298 K of Poly(methoxycarbonyl)cyclopentadienes in $CDCl_3$ and in $Cl_2CDCDCl_2$[a]

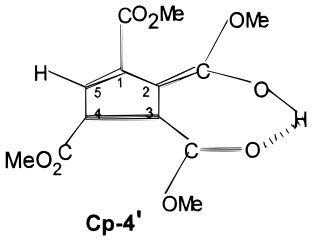
compd	^{1}H[b]	assignment	^{13}C	assignment	^{17}O	$\nu_{1/2}$ (Hz)	assignment
Cp-5	3.76 (3H)	MeO	51.8 (1C, q, J = 146.5 Hz)	MeO	130−135	1430	(OMe on C1−C5)
	3.90 (6H)	2MeO	52.5 (2C, q, J = 149.7 Hz)	MeO	225	650	(C=O/C−OH on C1,C2)
	4.03 (6H)	2MeO	55.5 (2C, q, J = 151.7 Hz)	MeO	ca. 325		(C=O on C4)
	20.09 (1H, br)[c]	enol-H	106.31	*C*-CO_2Me	ca. 353	2050	(C=O on C3,C5)
	3.69 (3H)[a]	MeO	117.86	*C*-CO_2Me			
	3.84 (6H)[a]	2MeO	133.66	*C*-CO_2Me			
	4.00 (6H)[a]	2MeO	163.10 (1C)	C=O			
	20.05 (0.8H)[a]	OH	167.69 (2C)	C=O			
	(0.16H)[e]						
			172.76 (2C)	C=O			
Cp-4	3.79 (3H)	MeO	51.35 (q, J = 146 Hz)	MeO	119	1240	OMe (on C1,C2)
	3.93 (3H)	MeO	52.46 (q, J = 147 Hz)	MeO	ca. 134		OMe (on C3,C4
	4.01 (3H)	MeO	54.86 (q, J = 149 Hz)	MeO	222	400	C=O/C−OH (on C1,C2)
	4.06 (3H)	MeO	55.04 (q, J = 149 Hz)	MeO	320	580	C=O (on C4)
	7.55 (1H)	ring H	107.13, 109.17	*C*-CO_2Me	349	360	C=O (on C3)
			110.64, 134.30	*C*-CO_2Me			
	19.80 (1H, br)	enol-H	128.95 (d, J = 174.2 Hz)	*C*-H			
	3.72 (3H)[a]	MeO	164.24 (1C)	C=O			
	3.86 (3H)[a]	MeO	168.42 (1C)	C=O			
	3.97 (3H)[a]	MeO	171.67 (1C)	C=O			
	4.01 (3H)[a]	MeO	172.69 (1C)	C=O			
	7.49 (1H)[a](0.29H)[d]	ring H					
	19.84[a](0.9H)	enol-OH					
	(0.71H)[e](0.17H)[d]						
Cp-3	3.80 (3H)	MeO	51.04 (1C, q, J = 146.3 Hz)	MeO	117.5	985	OMe (on C1,C2)
	4.02 (6H)	2MeO	54.37 (2C, q, J = 148.8 Hz)	MeO	ca. 135	Shoulder	OMe (on C4)
	7.63 (2H)[f]	ring H	109.90 (t, J = 6.2 Hz)	*C*-CO_2Me	221 (2O)	400	C=O/C−OH (on C1,C2)
	19.70 (1H, br)[c]	enol-OH	121.74	*C*-CO_2Me	311 (1O)	590	C=O (on C4)
			129.91 (dd, ^1J = 172 Hz, ^2J = 7.5 Hz)	*C*-H			
			165.49	C=O			
			172.33	C=O			

[a] In $Cl_2CDCDCl_2$ at 298 K. [b] All signals are singlets unless otherwise stated. [c] Disappears in D_2O. [d] In $Cl_2CDCDCl_2$ at 360 K. [e] At 330 K. [f] Integrates for 1.3H after shaking for a short time with D_2O in $CDCl_3$.

short and strong and hence contribute to the stability of the enols. (c) The ring C1−C2 bond, connecting the two enolic "esters" groups, is longer (1.431−1.453 Å) than other C−C bonds in the ring (1.386−1.410 Å). (d) For **Cp-4** there are potentially two enols with different hydrogen bonding arrangements. One terminal involving the C1−CO_2Me and C2−CO_2Me groups (**Cp-4**) and another internal and more symmetrical involving the C2−CO_2Me and C3−CO_2Me groups (**Cp-4′**). The observed structure is the first one.



Cp-4



Cp-4'

This may be due to a steric effect since the crowding around the hydrogen bonded planar moiety is higher for **Cp-4** which is surrounded by two, rather than one CO_2Me groups. (e) Whereas the enol moiety is planar with the ring, its neighbor CO_2Me groups are perpendicular to the ring plane. The next CO_2Me group is again in the ring plane, so that except for the two enolic CO_2Me groups which are in the same plane, all neighboring CO_2Me groups are perpendicular to one another.

Solid State ^{13}C NMR Spectra of Cp-5, Cp-4, and Cp-3. The chemical shifts derived from the CP-MAS solid state ^{13}C NMR spectra of **Cp-3**−**Cp-5** are given in Table 2. **Cp-5** displays four MeO signals including one at 51.9 ppm, which is probably for two carbons since it has higher intensity than the other signals. The observation of only three C=O signals may reflect a reduced number of signals by symmetry. However, three other low intensity signals at δ 127.6, 133.7, and 134.9 ppm are also observed at the same δ value at both 4 and 6 kHz. The latter two signals could be assigned to the two vinylic hemiacetal carbons C=C(OH)OMe of the enolic moiety. We did not assign the other low intensity signal.

For **Cp-4** four signals are clearly observed and an additional one at δ 123.5 ppm is clearly observed at 4 kHz and is broad at 6 kHz. The full number of signals is observed for **Cp-3** with those at δ 113.4 and 128.9 appearing with low resolution.

The MeO signals at δ 54.7 in **Cp-3**, 54.9 in **Cp-4**, and 53.4 in **Cp-5** were ascribed to those of the enol moiety, whereas those at δ 58.6 of **Cp-4** and 56.0 for **Cp-5** are ascribed to the ester group tilted out of the ring plane.

The most significant comparison is the difference (ΔS_{sol}) of these values from those of **Cp-3**−**Cp-5** in $CDCl_3$ (Table 3). For six signals of **Cp-3** in solution, ΔS_{sol} = 0.1−0.4 ppm and only for that at δ ($CDCl_3$) 129.9 ΔS_{sol} = 1.03 ppm. Four signals in the solid have no parallel in solution. For **Cp-4**, ΔS_{sol} < 0.8 ppm for 10 signals, 1.3 ppm for that at δ($CDCl_3$) 119.6, and is large for one signal (3.78 ppm). For seven signals of **Cp-5** in solution ΔS_{sol} < 1 ppm and for the two others ΔS_{sol} = 1.37 and 3.8 ppm.

The resemblance of the solid spectra, with few exceptions, to those in $CDCl_3$ suggests similar structures, i.e., an enolic structure in $CDCl_3$ solution.

Structure in Solution. There are some differences between the spectra in low dielectric chlorinated solvents and in more polar solvents.

Table 4. NMR Spectra (δ in ppm) of Poly(methoxycarbonyl)cyclopentadienes in CD_3CN at Room Temperature

compd	^1H[a]	assignment	^{13}C	assignment	^{17}O	$\nu_{1/2}$ (Hz)	assignment
Cp-5	3.92 (br)	5 OMe	53.22	OMe (q, J = 150 Hz)	ca. 135	1100	OMe
	3.86[b]	5 OMe	168.38 (br)	C═O	ca. 327	2650	C═O
	19.39 (v br)	OH (trace)	51.97[b]	OMe			
	20.13 (v br)[b]	0.68 H	54.88[b]	OMe			
	3.6[c]	5 OMe	171.83 (vw)[b]	C═O			
	3.6 (15H)[d]	5 OMe					
	12.25 (1H, br)[d]	acidic-H	50.69 (J = 146 Hz)[c]	OMe			
			116.3[c]	C-ring			
			166.5[c]	C═O			
			50.78 (q, J = 145 Hz)[d]	OMe			
			117.47[d]	C-ring			
			167.67[d]	C═O			
Cp-4	3.91 (12H, br)	4 OMe	52.73 (v b)	OMe			
	3.68, 3.80	4 OMe	106.80 (v sm)	*C*−CO_2Me			
	3.88, 3.99[b]		108.96 (v sm)	*C*−CO_2Me			
	7.41 (1H)	ring H	117.98 (v sm)	*C*−CO_2Me			
	7.32 (1H)[b]	ring H	127.57 (d, J = 173 Hz)	C−H			
	19.87 (1H,b)	acidic-H	133.23 (v sm)	*C*−CO_2Me			
	19.92 (1H)[b,e]		ca. 164 (v br)	C═O			
	3.54 (12H)[c]	4 OMe	ca. 168 (v br)	C═O			
	6.65 (1H)[c]	ring H	ca. 173 (v br)	C═O			
			50.69 (q, J = 146 Hz)[b]	OMe			
			51.72 (q, J = 146 Hz)[b]	OMe			
			54.92 (q, J = 150 Hz)[b]	OMe			
			55.04 (q, J = 150 Hz)[b]	OMe			
			106.74[b]	*C*−CO_2Me			
			108.98[b]	*C*−CO_2Me			
			117.97[b]	*C*−CO_2Me			
			126.70 (d, J = 173 Hz)[b]	C−H			
			133.28[b]				
			163.45[b]	C═O			
			167.60[b]	C═O			
			171.42[b]	C═O			
			172.76[b]	C═O			
			49.82 (q, J = 146.1 Hz)[c]	OMe	124	1080	OMe (on C1,C2)
			50.47 (q, J = 144.8 Hz)[c]	OMe	135−40		OMe (on C3,C4)
			111.63[c]	*C*−CO_2Me	221	860	C═O/C−OH (on C1,C2)
			119.37 (d, J = 164 Hz)[c]	C−H	321	1000	C═O (on C3)
			165.18[c]	C═O	359	810	C═O (on C3,C4)
			167.53[c]	C═O			
Cp-3	3.73 (3H)	OMe	50.45 (q, J = 146 Hz)	1 MeO	118	700	OMe (on C1,C2)
	4.01 (6H)	2 OMe	54.57 (q, J = 149 Hz)	2 MeO	135		OMe (on C4)
	7.43 (2H)	ring H	110.10 (m)	*C*−CO_2Me	221	340	C═O/C−OH (on C1,C2)
	19.70 (1H, b)	acidic-H	121.31 (vw, m)	*C*−CO_2Me	324	370	C═O (on C4)
	3.74 (6H)[c]	OMe	121.40	*C*−CO_2Me			
	3.61 (3H)[c]	OMe	128.64 (dd, ^1J = 171 Hz, ^2J = 7 Hz)	C−H			
	7.07 (2H)[c]	ring H	164.88	1 C═O			
	3.84 (9H)[f]	OMe	172.57	2 C═O			
			48.57 (q, J = 138.5 Hz)[c]	OMe			
			49.95 (q, J = 145.7)[c]	OMe			
			51.48 (q, J = 146.4 Hz)[c]	OMe			
			109.34[c]	*C*−CO_2Me			
			114.86[c]	*C*−CO_2Me			
			116.00[c]	*C*−CO_2Me			
			123.31 (d, J = 138.18 Hz)[c]	ring H			
			125.13 (d, J = 142.85 Hz)[c]	ring H			
			165.51[c]	C═O			
			166.05[c]	C═O			
			169.94[c]	C═O			

[a] All signals are singlets unless otherwise stated. [b] At 240 K. [c] In DMSO-d_6. [d] In DMF-d_7. [e] Sharp signal. [f] In D_2O.

(a) In Chlorinated Solvents. (i) ^{17}O NMR Spectra in $CDCl_3$. The ^{17}O spectra are probably the best tool for distinguishing unequivocally between the acid, enol, and cyclopentadienide structures, since at least one type of oxygen appears at a different δ for each structure. Moreover, in the hydrogen bonded enol structure the OH and the C═O oxygens become nearly or completely equivalent.

The number of signals in the ^{17}O NMR spectra for **Cp-5, Cp-4**, and **Cp-3** in $CDCl_3$ (Table 3) is dependent on the number of CO_2Me groups and signals appear in three regions: δ 117.5−135 (MeO), δ 311−353 (C═O), and δ 221−225 (═C−O−H). The MeO signals are broad and sometime overlap. Only one $Me^{17}O$ signal appears in the final spectrum of **Cp-5**, although in the absence of exchange the enol MeO groups reside in three different environments.

The two highest field (δ 119, 117) MeO groups were ascribed to those on C1 and C2 of the enolic unit, whereas MeO groups of normal methyl esters appear at δ 134, 135. Hence the MeO signals at 130−135 ppm for **Cp-5** raise a possibility of exchange of the two MeO groups

which may be supported by the broader signal ($\nu_{1/2}$ = 1430 Hz) than of other MeO signals. However, we observed relatively early in the accumulation a second MeO signal at ca. 125 ppm, but only one C═O signal at ca. 353 ppm. This might mean that all the nonenolic ester groups were initially orthogonal to the cyclopentadiene ring or that the C═O signal at C4, expected to be at ca. 320 ppm if conjugated, had not been observed due to its low intensity coupled with a very low signal-to-noise ratio.

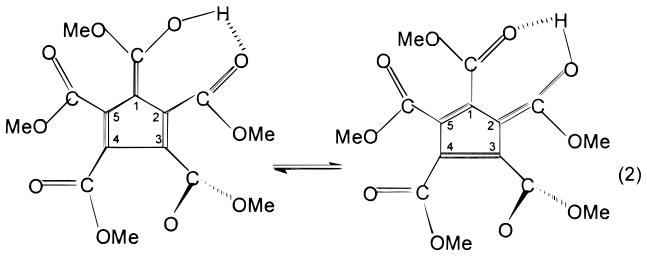
The Me*O* signals at 117 and 135 ppm of **Cp-3** partially overlap, but since δ 135 is a shoulder, a tentative 2:1 ratio is reasonable. The C4-ester group is planar with the ring system, as deduced by comparing its δ values with those of RC_6H_4COOMe, R = H, *p*- and *o*-MeO.[17a]

The C═^{17}O signals appear as two subgroups. At δ 311, 320 are C═O groups remote from the enolic moiety which are conjugated to the cyclopentadiene ring. The C═O groups flanking the enolic moiety and orthogonal to the ring appear at 349, 353 or at 349−359. A very broad signal comprising both regions appears at ca. 325 (C3, C5) and ca. 353 (C4) for **Cp-5**. This may be due to the increased molecular weight and to partial overlap of the two different C═O signals.

These assignments are based on analogies. The MeO signals are in the reported range for methyl esters,[17b] many of which are near 135 ppm. The most upfield signals at the narrow range of δ 117.5−124 are thus assigned to the ═C(OH)*O*Me group. The C═O signals are in the range of the literature values for ester groups, particularly those bound to electron-rich unsaturated systems.[17c]

The signal with an approximate intensity of two oxygens, appearing at the *new* region of δ 221−225, indicate the presence of a new functionality, with two nearly identical oxygens which are at approximately the same environment in the three species. This signal is ascribed to the enol of ester oxygens, formerly belonging to the enolic ^{17}OH and a formally neighboring C═O. Since they display the same δ value, a symmetrical strong hydrogen bond O···H···O which is not very sensitive to the environment is indicated.

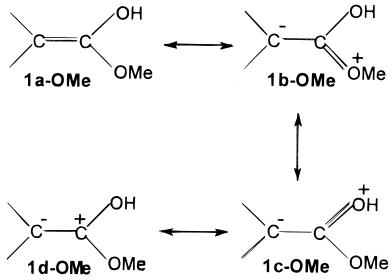
Many enolic δ(^{17}O) values are significantly upfield compared with our values.[18] However, those for $CHAc_3$, 2-acyl-1,3-cycloalkanediones, 5-acyl-Meldrum's acid, and 5-acyl-1,3-dimethylbarbituric acid are at δ 188−256 ,[19a] and in ascorbic acid enolate δ(^{17}O) = 216.[19b] A similar range was observed in several enols of simple β-diketones.[20] The deshielding of the enolic OH has been attributed to "the positive charge on oxygen".[19a] We ascribe the strong deshielding in our enols to three reasons. First, to electron withdrawal by the CO_2Me groups which reduces the electron density at the oxygen, in agreement with Bolvig et al.[19a] Second, similarly to the hydrogen bonded β-diketones, where due to the tautomerization between two enolic forms the δ(OH) values are at low field,[20] our enolic OH group is also hydrogen bonded to a neighboring ester C═O. Whether this H-bond is a single minimum or the two forms (demonstrated for **Cp-5** in eq 2) tautomerize rapidly, the



(2)

two oxygens are equivalent on the ^{17}O NMR time scale, and only one signal, with δ value between those for the C═O and OH groups, is observed. This conclusion fits with the nearly symmetrical hydrogen bond observed in the solid state (Table 1). Third, to the "push" effect discussed below.

Since vinylic MeO groups are at δ 30−60 with the most deshielded one at 68 ppm,[21] values which are much upfield compared with our ca. 220 ppm signals, these signals *must* be assigned to the enolic OH. Both oxygens of the ═C(OH)(OMe) moiety are strongly deshielded. We ascribe it to resonative electron-donation ("push") by the two oxygens in our push−pull systems which increases the C−O bond order with a consequent deshielding. By describing the enolic moiety with resonance structures **1a-OMe**−**1d-OMe**, δ(OH) and δ(OMe) are rationalized by the Karplus−Pople[22] equation. The positive charge, reducing the p orbitals volume r^{-3} term, and the increased π bond order, influencing the ΣQ_{Ox} term, cause deshielding.



(ii) ^{1}H NMR Spectra. (1) In $CDCl_3$. The ^{1}H NMR signals in $CDCl_3$ (Table 3) appear in three regions: the MeO, the vinylic-H, and the enolic-OH. **Cp-5** displays 3 OMe signals in 1:2:2 ratio, in line with the enol of ester structure. Two identical MeO signals are attached to the O···H···O moiety at C1 and C2, and two identical, probably perpendicular, C3,C5-CO*OMe* groups flank this moiety. The separate signals indicate the absence of a fast consecutive proton migration between neighboring CO_2Me groups on the ring which will lead to a rapid exchange on the ^{1}H NMR time scale at room temperature.

(17) Boykin, D. W.; Baumstark, A. L. In *^{17}O NMR Spectroscopy in Organic Chemistry*; Boykin, D. W., Ed.; CRC Press: Boca Raton, 1991; Ch. 8, pp 217, 220−2, and references therein.

(18) Frey, J.; Eventova, I.; Rappoport, Z.; Müller, T.; Takai, Y.; Sawada, M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 621 and references therein.

(19) (a) Bolvig, S.; Duus, F.; Hansen, P. E. *Magn. Reson. Chem.* **1998**, *36*, 315. (b) Ruchmann, A.; Lauterwein, J.; Bäcker, T.; Klessinger, M. *Magn. Reson. Chem.* **1996**, *34*, 116.

(20) Gorodetsky, M.; Luz, Z.; Mazur, Y. *J. Am. Chem. Soc.* **1967**, *89*, 1183.

(21) Taskinen, E.; Hellman, J. *Magn. Reson. Chem.* **1994**, *32*, 353. (b) Kalabin, G. A.; Kushnarev, D. F.; Valeyev, R. B.; Trofimov, B. A.; Fedotov, M. A. *Org. Magn. Reson.* **1982**, *18*, 1.

(22) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803.

(23) Floris, B. In *The Chemistry of Enols*; Rappoport, Z., Ed.; John Wiley: Chichester, 1990; Chap. 4, p 147.

(24) For a review of rearrangments in X-substituted penta(methoxycarbonyl)cyclopentadienes, X = O_2NAr, carbonyl group, or amidine, see Lukyanov, S. M.; Kublik, A. V. In *The Chemistry of Dienes and Polyenes*; Rappoport, Z., Ed.; Wiley: Chichester; Vol. 2, in press.

We assign the signal at δ 4.03 to the C1,C2-CO*OMe* groups. The single MeO group is at δ 3.76, and if we assume that δ decreases with the increased distance from the enol group, δ 3.90 is assigned to the C3,C5-CO*OMe* groups. The assumption is corroborated by the δ(MeO) values in **Cp-4** and **Cp-3** (see below).

Cp-4 displays four MeO signals, thus excluding the symmetrical enol **Cp-4′**. In **Cp-4** the C1, C2−CO_2Me groups (at δ 4.01, 4.06) form the enol moiety, and the four groups are in different environments. **Cp-3** is symmetrical with the C1,C2-CO_2Me groups at δ 4.02, and a C4-CO_2Me at δ 3.80 in line with the generalization.

Strong evidence for the enolic structure is the appearance of a somewhat broad single ring hydrogen in **Cp-5**−**Cp-3** at δ 19.7−20.1. This contrasts the reported value for **Cp-5** at δ($CDCl_3$) 31.10.[9b] This low field δ value which is in the range of some enols of β-diketones[23] but is at a lower field than the δ(OH) of YY′C═C(OH)NHPh (Y,Y′ = CO_2R, CN)[6] is consistent with a strongly hydrogen bonded enol. When samples of enols **Cp-5**−**Cp-3** in $CDCl_3$ are shaken with D_2O for 1−5 min, the OH signal completely disappears. With **Cp-4** the ring C−H signal at δ 7.55 nearly retains its intensity after 2 min, whereas the 2H ring C−H signal of **Cp-3** at δ 7.61 partially exchanges since it integrates for 1.3H.

(2) In $Cl_2CDCDCl_2$. For **Cp-5** in $Cl_2CDCDCl_2$ the spectrum at 298 K resembles that in $CDCl_3$ with an 1 (OH): 6 (2 MeO): 6 (2 MeO): 3 (MeO) ratio. At 330 K the OH and MeO signals broaden and the OH intensity decreases; at 360 K the OH signal is very broad and the MeO signals nearly merge to a broad signal centered at δ 3.89. On recooling to 298 K after 18 min, the original spectrum reappears, with additional 0.16 H signal at δ 19.85, and three signals at δ 3.38−3.99 (ca. 15% of the overall MeO region intensity).

For **Cp-4** at 330 K the only difference from 298 K is a reduced intensity of δ(OH). At 360 K the intensities of the OH and the ring H signals decrease strongly and many additional small signals are formed (Table 3). On recooling to room temperature, the OH signal is of 0.76H intensity and at least eight new signals (of ca. 10% of the overall intensity) at δ 3.69−4.10 and a signal at δ 18.64 (0.05H) are observed.

For **Cp-3** a 1:2:6:3 ratio of the OH (δ 19.68), C−H (δ 7.56), MeO (δ 3.99, 3.74) is observed at 298 K. Broadening, especially of δ(OH), occurs at 360 K. On recooling to 298 K, new signals, e.g., at δ 19.98 (0.08 H) are observed in addition to the old ones.

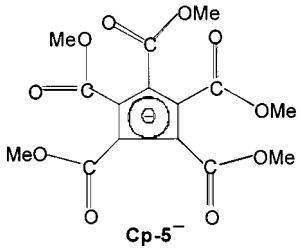
We interpret these changes as due to slow rearrangments[24] or decomposition processes at 298 K which become faster at the higher temperature. On cooling, the "new" higher temperature equilibrium is frozen. All the reactions generate new signals at > δ 19.6 and are discussed further below.

^{13}C NMR. (a) In $CDCl_3$. The number of ^{13}C signals corresponds to that of the ^{1}H signals. There are three signals each for the MeO, ring C, and C═O of **Cp-5**, four signals each for the MeO, ring C, and C═O of **Cp-4**, and two signals each for the MeO, ring C, and C═O groups of **Cp-3**. The MeO signals and the H−C coupling constants in the MeO group decrease consistently but only slightly when the CO_2Me group is more remote from the enolic center.

The "carbonyls" of the enolic moiety appear at lower δ(C═O) values than usual C═O signals. This is important, since we found previously[6] that C_α signals of enols of amides also appear in this region. This was ascribed to structures similar to **1b-OMe**−**1d-OMe**, where C_α-(OH)(OMe) carries an extensive partial positive charge. Consequently, the conclusions drawn from the ^{1}H NMR spectra are strengthened.

(b) In Polar Solvents. In much more polar solvents than $CDCl_3$, i.e., CD_3CN, DMSO-d_6, or DMF-d_7 the NMR spectra not always correspond to the solid-state structure and some similarities between the various species are lost.

(i) ^{17}O NMR Spectra. In CD_3CN, **Cp-5** displays only one ^{17}OMe signal at δ ca. 135 and a very broad C═O signal at δ 327. Consequently, all the CO_2Me groups are identical. The most likely (and previously suggested[9b]) structure is the symmetrical pentakis(methoxycarbonyl)-cyclopentadienyl anion **Cp-5**$^-$: "orthogonal" ester groups are absent and planarity with conjugation of all CO_2Me groups should be achieved by increased steric hindrance. Since the δ's resemble those in $CDCl_3$, a *substantial* negative charge delocalization into the ester groups is unlikely. The very broad C═O signal suggests a possible exchange with a species present at low percentage, e.g., **Cp-5**.



Cp-5$^-$

In contrast, the spectra of **Cp-4** and **Cp-3** resemble, with a few ppm difference, those in $CDCl_3$. **Cp-4** displays two MeO and two C═O signals and an OH signal at 221 ppm. **Cp-3** displays two MeO and one C═O signal, and an OH signal at 221.3. Hence, the structures of **Cp-4** and **Cp-3** in CD_3CN are, like in $CDCl_3$, those of the enols of esters.

(ii) ^{1}H NMR Spectra. A similar conclusion is deduced from the ^{1}H NMR data in CD_3CN. **Cp-5** displays only one MeO signal, and the spectrum of **Cp-3** resembles that in $CDCl_3$. For **Cp-4**, since only one broad MeO signal appears for the four groups, overlap (or even exchange of two species) may lead to an accidental identity of the groups. One ring hydrogen is observed, but a broad ^{1}H signal at δ 19.71 is indicative of an enolic structure.

In DMSO-d_6 and DMF-d_7 **Cp-5** displays only one MeO signal at δ 3.6. In DMF-d_7 a broad 1H signal, which may be a protonated DMF, is also observed at δ 12.25. In DMSO-d_6 **Cp-4** displays one MeO signal at δ 3.54 and one ring proton, but the acidic proton is not observed. **Cp-3** showed two MeO and one ring H signals, but no acidic proton. It is clear that **Cp-5** ionizes, but the situation is not entirely clear for **Cp-3**.

The rt spectrum of **Cp-4** in DMF-d_7 displays on dissolution a broad 0.9H OH signal at ca. δ 15.3, one 1H signal at δ 6.88 (ring H) and MeO signals at δ 3.61 and δ 3.65 (6H each). Fourteen minutes later, new signals were observed at δ 3.64 (ca. 0.12H), 3.76, 3.77 (0.12H), and 7.21 (0.06H). After 1 h δ 7.21 and δ(OH) are 0.6H each.

For **Cp-3** in DMF-d_7 at room temperature the 3(MeO): 6(2 MeO): 2(ring H): 1(OH) signals at δ 4.00, 3.72, 7.36, and 15.70 were accompanied already after 12 min by new signals at δ 3.28, 3.65, 3.84, and 7.26. After 1 day, ten MeO signals were observed.

(iii) ^{13}C NMR Spectra. These are parallel to the ^{1}H NMR spectra. **Cp-5** shows only one CH_3O, one ring C, and one "C=O" signal (at δ 166.5) in DMSO-d_6, and similar signals in DMF-d_7. In contrast, **Cp-4** displayed in DMSO-d_6 two MeO, one ring-bound CO_2Me, a *C*-H, and two "C=O" signals. Again, the spectrum is intermediate between those of **Cp-4** and **Cp-4**$^-$, and their exchange seems likely.

1,2-Bis(methoxycarbonyl)cyclopentadiene (1,2-Cp-2). Pure **1,2-Cp-2** is unknown, although it may have been formed by protonation of its Na salt.[25] Bis-methoxycarbonylation of sodium cyclopentadiene with methyl chloroformate gave a mixture of sodium 1,2- and 1,3-bis-(methoxycarbonyl)cyclopentadienes, which on protonation gave a 2:3 mixture of their carbon acids.[12,13]

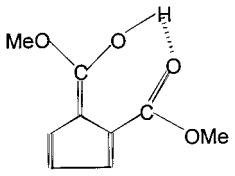
We repeated this procedure with several variations in order to obtain the pure 1,2-isomer. The literature ratio of 1,2- to the 1,3-sodium salts that we also obtained was 6:1, and fractional crystallization from MeOH raised this ratio to 9:1. Each salt showed one MeO and three ring H signals in the ^{1}H NMR spectrum. However, complete separation by fractional crystallization, preparative TLC, or column chromatography failed.

When the methoxycarbonylation time was extended, a 93:7 mixture of 1,2-$(CO_2Me)_2^-Na^+$ and 1,2,4-$(CO_2Me)_3^-Na^+$ was obtained. Preparative TLC gave pure **Cp-3**.

Protonation of the sodium salt of the 1,2-CO_2Me isomer can give four isomers: the enol **1,2-Cp-2-I**, the nonenolizable **1,2-Cp-2-II** and **1,2-Cp-2-III**, and the acid **1,2-Cp-2-IV**. Indeed, protonation of the 93% sodium **1,2-Cp-2** isomer gave an NMR spectrum consistent with a mixture of all isomers displaying six MeO signals at δ 3.69−3.98, two CH_2 signals at δ 3.25−3.45, one C*H*CO_2Me signal at δ 4.28, six ring CH signals at δ 6.17−7.37, and one OH singlet at δ 19.28. δ values at 298 K in 1:0.3 (v/v) CCl_4−$CHCl_3$ and assignments and percentages of the isomers are given below. In a similar experiment a somewhat different isomer ratio was obtained: **1,2-Cp-2-I** (8%): **1,2-Cp-2-II** (18%): **1,2-Cp-2-III** (37%): **1,2-Cp-2-IV** (37%).

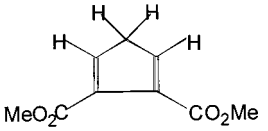
These assignments are based on the δ(^{1}H) values, the consistent relative integration of different signals for each isomer, and the signals in the proton-coupled ^{13}C spectra. The CH_2 groups of **1,2-Cp-2-II** and **1,2-Cp-2-III** show two triplets, whereas the ring carbon of the *C*HCO_2Me group of **1,2-Cp-2-IV** is a doublet. We assumed a lack of rearrangement of the CO_2Me groups to the 1,3-positions on protonation. This is important since, for example, **1,3-Cp-2** should also display a C*H*CO_2Me signal with characteristics similar to that in **1,2-Cp-2-IV**. Consequently, the spectra of the 1,2- and 1,3-$(CO_2Me)_2$ isomer mixture were investigated.

Protonation of a 2:1 mixture of the 1,2- to the 1,3-salts gave a complex ^{1}H NMR spectrum, and the numerous OMe signals suggest that the 1,3-salt also gives few isomers on protonation. Analysis of the ring C−H region was possible, although due to the complexity of the spectra and few nonresolved couplings, errors in the distribution are possible. In addition to signals of the 1,2-isomers, new signals were observed at δ 7.38 (t, J = 1.5 Hz), 7.46 (t, J = 1.5 Hz), and 7.62 (q). These signals appeared to be <10% in the protonation of the 93% 1,2-salt, excluding a rapid rearrangment to 1,3-isomers.



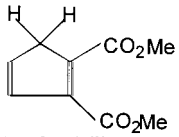
1,2-Cp-2-I

3.99 (6H, s, 2MeO)
6.17 (1H, t, J = 3.8 Hz, H4)
7.09 (2H, d, J = 3.8 Hz, H3, 5)
19.28 (1H, s, OH)
15%



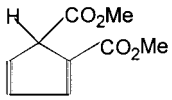
1,2-Cp-2-II

3.25 (2H, t, J = 1.4 Hz, CH_2)
3.82 (6H, s, MeO)
7.03 (2H, t, J = 1.4 Hz, H2, 5)
15%



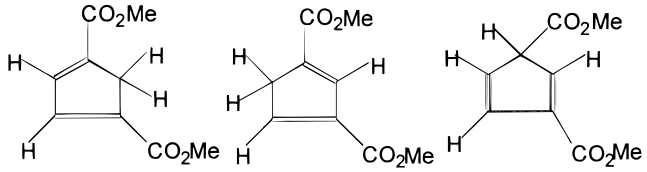
1,2-Cp-2-III

3.45 (2H, , CH_2)
3.787 (3H, s, OMe)
3.79 (3H, s, MeO)
6.59 (1H, m, H5)
7.37 (1H, s, H4)
25%



1,2-Cp-2-IV

3.69 (3H, s, MeO)
3.86 (3H, s, MeO)
4.28 (1H, , H1)
6.59 (1H, m, H4)
6.62 (2H, m, H3, 5)
45%



1,3-Cp-2-I **1,3-Cp-2-II** **1,3-Cp-2-III**

Three **1,3-Cp-2** isomers are expected: the nonenolizable **1,3-Cp-2-I**, and **1,3-Cp-2-II** with two CO_2Me groups conjugated with the ring, and the potentially enolizable **1,3-Cp-2-III** having one sp^3-C-connected ester group. The more symmetrical **1,3-Cp-2-I** should show three types of hydrogens, and the signals at δ 3.82 (s), 3.62 (t, J = 1.5 Hz), and 7.38 (t, J = 1.5 Hz) were ascribed to it. **1,3-Cp-2-II** should show two different MeO signals and three types of ring H, and the new signals at δ 3.89 (s), 3.83 (s), 3.51 (t, J = 1.5 Hz), 7.46 (t, J = 1.5 Hz) and 7.62 (q) were ascribed to it. From our data, **1,3-Cp-2-III** (with the expected 4 ring H and 2 MeO) was not formed. The product distribution is **1,2-Cp-2-I** (4%): **1,2-Cp-2-IV** (27%): **1,2-Cp-2-III** (27%): **1,2-Cp-2-II** (12%): **1,3-Cp-2-I** (15%): **1,3-Cp-2-II** (15%).

Significantly, no new enolic signal is formed at ca. 19.5 ppm.

The ^{13}C NMR spectrum in 4:1 (v/v) CCl_4:$CDCl_3$ show six weak C=O signals at δ 162.77−170.97 and fourteen ring carbons at δ 109.08−144.04. The hydrogen-coupled ^{13}C spectrum shows eight doublets (^1J = 169−177 Hz), one of which is a doublet of doublets (^2J = 4.3 Hz). The other signals are singlets. A signal at δ 57.93 (qxd, ^1J = 132 Hz, $^{2,3}J$ = 8.5 Hz) is clearly the C*H*CO_2Me signal of **1,2-Cp-2-IV**. The presence of six MeO q at δ 51.43−53.66, a *C*H_2 at δ 43.28 (txt, ^1J = 129 Hz, ^2J = 8.0 Hz), and at

(25) Peters, D. *J. Chem. Soc.* **1959**, 1761.

δ 40.96 (dxt, $J = 7.6$ Hz) are consistent with the presence of the four isomers **1,2-Cp-2-I**−**1,2-Cp-2-IV**.

Protonation of the 9:1 mixture of 1,2- and 1,2,4-salts at 0 °C gave a complex ^{1}H NMR spectrum which was analyzed as a five-isomer mixture in the following ratio: **Cp-3** (10%): **1,2-Cp-2-I** (20%): **1,2-Cp-2-II** (10%): **1,2-Cp-2-III** (30%): **1,2-Cp-2-IV** (30%).

The ^{17}O NMR spectrum of the **1,2-Cp-2** mixture after ca. 12 h displayed two signals: at 136 ppm ($\nu_{1/2} = 720$ Hz) and at 350 ppm ($\nu_{1/2} = 970$ Hz). However, at up to 1 h, three signals were observed: at 332 (disappearing with time) and 350 ppm and at 210 ppm (very faint, which may be the enolic OH, disappearing with time).The δ-(^{17}O) in the final spectrum resemble those of the non-enolic CO_2Me groups of **Cp-5**−**Cp-3**. The change in the δ(C═O) value is unclear but dimerization is a possibility.[25]

The small concentration of **1,2-Cp-2-I** rationalize the fact that an enolic signal was not, or only slightly, detected by the not too sensitive ^{17}O NMR technique.

Three conclusions arise from these experiments. First, protonation of the salt leads to all possible isomers of the 1,2-bis(methoxycarbonyl)cyclopentadienes. Second, in contrast with only the enolic structures of **Cp-3**−**Cp-5**, the two ester (**1,2-Cp-2-IV**, major)/enol(**1,2-Cp-2-I**, 5−20%) isomers exist independently on the ^{1}H and ^{13}C NMR time scales. Third, the low field δ(OH) of the enol in the ^{1}H NMR spectrum resembles that in the enols of **Cp-3**−**Cp-5**. We note that the lack of a rapid interconversion of **1,2-Cp-2-IV** and **1,2-Cp-2-I** is not unique. The anilides $XCH(CO_2R)CONHPh$, $X = CO_2Me$, $R = Me$; or $X = NO_2$, $R = Et$,[6] show at room temperature a small percentage of the enol of the anilide together with the main "amide" isomer.

Lack of Exchange of the Enolic OH Groups. The mixtures of the 1,2- and 1,3-isomers revealed no exchange of the enolic OH groups between two enols. Hence we investigated the δ(O^{1}H) region for other enol mixtures in $CDCl_3$. At 298 K a mixture of **Cp-3** and **Cp-5** show separately the broad OH signal of **Cp-5** at δ 19.96 and a sharp signal of **Cp-3** at δ 19.68. At 220 K both signals are sharp singlets at δ 20.27 and 19.94, respectively. In a mixture of **Cp-3** and **Cp-4** all signals are sharp. At 298 K $\delta = 19.90$ (**Cp-4**) and 19.73 (**Cp-3**), and at 220 K $\delta = 20.12$ (**Cp-4**) and 19.98 (**Cp-3**). These signals appear at the δ(OH) values of the pure enols, and we conclude that no observable interaction or exchange between the OH groups of different enols exists in their mixture.

IR Spectra. The IR spectra in the C═O region are very similar for **Cp-5** and **Cp-4**. In $CDCl_3$ $\nu_{max} = 1731$, 1711 cm^{-1} for **Cp-5**, and 1730, 1707 cm^{-1} for **Cp-4**, and 1736, 1711 (**Cp-5**), 1736, 1709 cm^{-1} (**Cp-4**) in CH_3CN. The ν_{max} are at lower wavenumbers for **Cp-3**: 1691 (in $CDCl_3$) and 1703 (in CH_3CN) cm^{-1}. All the enols show weak signals at ca. 3400 cm^{-1} and a continuous increase in absorption at 3000−2400 cm^{-1} which we ascribed to the hydrogen bonded moiety. Similar values were observed in CCl_4 where ν_{CO} (cm^{-1}): 1728, 1712, 1672 (**Cp-5**), 1705, 1700 (**Cp-4**) and 1697 (**Cp-3**).

Activation by the Ester Groups. When 5-, 4-, and 3-methoxycarbonyl groups substitute a cyclopentadienyl moiety, the ester group on the sp^3-hybridized carbon and its neighboring ester group form in the solid state exclusively a *symmetrical* enolic moiety with characteristic bond lengths (Table 1).

The solid-state CP-MAS spectra of **Cp-3**−**Cp-5** bridge between the X-ray diffraction data and the solution ^{13}C spectra. The near identity with the ^{13}C NMR data in $CDCl_3$ solution, the ^{1}H and ^{17}O NMR data, and the number of signals, δ, and J values in $CDCl_3$ are consistent with the enol of ester structures. One of the isomers of the 1,2-diester in $CDCl_3$ is the enol **1,2-Cp-2-I**, but the main isomer is the diester form **1,2-Cp-2-IV**. Hence, the presence of only two methoxycarbonyl groups reduces the gap between the stabilities of the ester and enol isomers to within 1 kcal/mol.

Mono(methoxycarbonyl)cyclopentadiene is known only as its dimer at room temperature[25,26] and, although the monomeric enol form was drawn,[25] there is no evidence for its structure. However, the enol **1,3-Cp-2-III** which has an sp^2-hybridized enolizable CO_2Me group, is not observed among its isomers. The difference from **1,2-Cp-2-I** suggests that a single methoxycarbonyl group on a cyclopentadiene does not enolize to a significant extent and emphasizes the dominant role of intramolecular hydrogen bonding in stabilizing the enols. Indeed, the hydrogen bond distances in the solid **Cp-3**−**Cp-5** classify them as strong hydrogen bonds.[27]

In contrast, for tris(methoxy [or ethoxy] carbonyl)-methane with three geminal ester groups both the ^{1}H NMR spectra and theoretical calculations[6] indicate that the triester form is several orders of magnitude more stable than the enol form. Consequently, the electron-withdrawing cyclopentadiene moiety increases K_{enol} enormously, although repulsion between the close COO dipoles of the three geminal ester groups destabilize the triester form relative to the enol.

Ionization in Polar Media. The high acidity of the enol form is expected to lead to ionization in a high dielectric solvent, thus losing the "enol" characteristics. Apparently, this does not occur even with the most acidic **Cp-5** in the low dielectric solvents $CDCl_3$ or $Cl_2CDCDCl_2$ at room temperature. However, this partially happens in the more polar and more basic solvents CD_3CN, DMSO-d_6, and DMF-d_7. The most acidic **Cp-5** ionizes completely to its anion **Cp-5**$^-$ as shown by the single CO_2-Me group signal. This is not observed with the less acidic **Cp-3** whereas **Cp-4** displays an intermediate behavior: an incomplete ionization to the **Cp-4**$^-$ ion, which probably exchanges with another species, e.g., the un-ionized **Cp-4**, leads to signal broadening.

Side Reactions. Two experimental problems which complicate the analysis are decomposition and rearrangments. Many systems CHYY′Y″ (Y, Y′, Y″ = EWGs) decompose in solution.[6] The change in the NMR spectra of our polyester systems in DMF at room temperature or in $Cl_2CDCDCl_2$ at 330−360 K can be due, at least partially, to this reason.

Cyclopentadienyl systems can undergo rearrangments,[24] three of which can be visualized in our systems. (1) The enolic hydrogen can migrate from the $H(CO_2Me)_2$ moiety to a neighboring CO_2Me group which, coupled with accompanying double bond migration in the ring, will generate a new enol. This migration, which can cover all five CO_2Me groups, is degenerate for **Cp-5**, but it can lead to line broadening in the NMR spectrum. For enol **Cp-4** (on C1,C2-CO_2Me) this can lead to an internal enol

(26) Peters, D. *J. Chem. Soc.* **1961**, 1042.
(27) Perrin, C. L.; Nelson, J. B., *Annu. Rev. Phys. Chem.* **1997**, *48*, 511.

on the C2,C3-CO_2Me groups (**Cp-4′**). Depending on the rearrangment rate, line broadening and appearance of signals of the new enol are possible. **Cp-3** cannot undergo this reaction. (2) An enol/ester tautomerization, by a sequence of enol ionization followed by ring protonation, can lead to various nonenolic isomers, e.g., to **1,2-Cp-2-III** and **1,2-Cp-2-IV** from **1,2-Cp-2-I**. (3) 1,2-CO_2Me migration. This may convert **Cp-3** to its 1,2,3-isomer.

Rearrangment involving a "proton walk" around the periphery of the ring was not observed in $CDCl_3$ or Cl_2-$CDCDCl_2$ at room temperature probably due to two reasons. First, the strongly hydrogen bonded moiety in the ring plane stabilizes the enol, and migration to a neighboring perpendicular CO_2Me group requires energy for the conformational change. Second, the initial ionization required for this migration is not favored in the low dielectric solvents at room temperature.

However, the observations of line broadening and appearance of new compounds, including enolic ones, at higher temperature in $Cl_2CDCDCl_2$ could be rationalized since at the higher temperature the initial ionization is faster. The analysis above accounts for the results for **Cp-4** in term of route 1, whereas route 2 could apply to **Cp-3**. A new enol cannot be formed for **Cp-5** but decomposition to a cyclopentadiene with a smaller number of CO_2Me groups can account for the new OH signal.

Ionization is a major reaction at room temperature in DMF, so that rearrangments are facile and the observed new signals for **Cp-3** and **Cp-4** can be ascribed to the routes mentioned above.

Conclusions. The present results extend the meager data hitherto available on enols of esters and give examples of compounds existing as such enols both in the solid state and in solution. They give the scope of activation required for formation and observation of such enols when the degree of activation is regularly modified and point to the possibility that the enol moiety may ionize in a polar medium.

Experimental Section

General Methods. The equipment used was described earlier.[28]

^{13}C CP-MAS Spectra. These were recorded at room temperature using a Varian UNITY INOVA spectrometer with a 9.39 wide bore magnet operating at 100.576 MHz. The measurements were performed with a probe having a 7 mm zirconia rotor, at spinning rates of 4 and 6 kHz. Typical parameters were as follows: 500 transients; spectral width, 50000 Hz; 1024 data points; contact time, 8 ms; recycle delay 4s.

^{17}O NMR Spectra. ^{17}O NMR spectra were recorded, in the Fourier transform mode, on a spectrometer equipped with a 10 mm broad band probe at 298 K at natural isotopic abundance. Saturated solutions were used in all experiments. The instrumental settings were as follows: 40.662 MHz frequency, spectral width 36 kHz, acquisition delay 100 μs, pulse angle 90° (pulse width 28 μs). Number of scans varied largely (4×10^5 to 6×10^6) as a function of solvent and solubility. The spectra were recorded with sample spinning and without lock. The signal-to-noise ratio was mostly improved by applying a 30 Hz exponential broadening factor (l.b.) to the FID prior to Fourier transformation. In some experiments an l.b. up to 120 Hz was necessary. The data point resolution was improved by zero filling to 16 K data points. Chemical shifts (ppm) are referred to external tap water by the substitution method. The δ's reproducibility is estimated to be $\pm$1 ppm ($\pm$3 ppm for l.b. = 120 Hz).

Solvents and Materials. All the deuteriated solvents used for the NMR measurements were commercial and were used without further purification.

1,2,3,4,5-Pentakis(methoxycarbonyl)cyclopentadiene (Cp-5). Cp-5, mp 146−8 °C, ^{1}H NMR ($CDCl_3$) δ: 3.78−4.04 (15H, 3s, CO_2Me), 20.01 (1H, br s, enolic H), lit:[9b] 3.95 (br, MeO), 31.10 (OH), was prepared according to the literature.[9b]

1,2,3,4-Tetrakis(methoxycarbonyl)cyclopentadiene (Cp-4). To a solution of potassium pentakis(methoxycarbonyl)-cyclopentadiene (2 g, 5.1 mmol) in MeOH (25 mL) was added KOH (0.5 g, 10.6 mmol, 1:2 molar ratio of reagents) in MeOH (10 mL) at room temperature, and the mixture was stirred for 2 h. After 2 weeks, yellowish crystals precipitated. Washing with MeOH gave 0.88 g of potassium 1,2,3,4-tetrakis(methoxycarbonyl)cyclopentadienide.

When a 1:1 molar reagent ratio was kept for 1 day at room temperature or refluxed for 4 days in MeOH, no reaction took place.

The solid (0.88 g) was dissolved in water (5 mL), and concentrated HCl (3 mL) was added slowly, until a complete precipitation of a white solid (0.46 g, 56%). Recrystallization (MeOH) gave **Cp-4** as a white solid which turns red on heating and starts to decompose at ca. 152−3 °C. ^{1}H NMR ($CDCl_3$) δ: 3.82, 3.93, 4.01, 4.06 (4 × 3H, 4s, CO_2Me), 7.56 (1H, s, ring H), 19.90 (1H, s, OH). Anal. Calcd for $C_{13}H_{14}O_8$: C, 52.30; H, 4.70. Found: C, 52.30; H, 4.77.

(b) To a solution of $K(C_5(CO_2Me)_5)$ (2.2 g, 5.58 mmol) in water (5 mL)−MeOH (10 mL) was added slowly a KOH solution (0.31 g, 5.54 mmol) in MeOH (5 mL). The mixture was stirred for 2 h, and the solid obtained was identified as the precursor.

(c) To a solution of the methanolate $K(C_5(CO_2Me)_5)\cdot$MeOH (1.25 g, 2.9 mmol) in DMF (5 mL) was added slowly at ice−water temperature a solution of KOH (0.16 g, 2.9 mmol) in MeOH (2 mL) (molar ratio 1:1), and the mixture was allowed to stand for 24 h. Ether was added, and the solid obtained (1 g) was washed with MeOH, giving 0.6 g of a solid which was dissolved in water (3 mL). Concentrated HCl (ca. 3 mL) was added until a complete precipitation of a white solid. Recrystallization (MeOH) gave 0.1 g of **Cp-4**.

(d) To a solution of the methanolate $K(C_5(CO_2Me)_5)\cdot$MeOH (1 g, 2.3 mmol) in water (3 mL) was added slowly a solution of KOH (0.13 g, 2.3 mmol) in water (1 mL) at 0 °C, and the mixture was allowed to stand for 2 weeks at room temperature. Concentrated HCl (3 mL) was slowly added until a complete precipitation of a white solid. After filtration and drying, **Cp-4** (0.5 g, 71%) was obtained. Crystallization (MeOH) gave 0.3 g (43%).

1,2,4-Tris(methoxycarbonyl)cyclopentadiene (Cp-3). To a solution of $K(C_5(CO_2Me)_5)$ (2 g, 5.08 mmol) in water (8 mL) was added a solution of KOH (0.67 g, 11.9 mmol) in water (3 mL) (molar ratio 1:2). The mixture was allowed to stand for two weeks at room temperature. Concentrated HCl was added dropwise (5 mL) until a complete precipitation of a solid (800 mg, 65%). Recrystallization (MeOH) gave a white solid, mp 118−9 °C (400 mg, 50%) which was identified as **Cp-3** by its NMR spectra. ^{1}H NMR ($CDCl_3$) δ: 3.82 (3H, s, CO_2Me), 4.01 (6H, s, $2CO_2Me$), 7.65 (2H, s, ring H), 19.73 (1H, s, enolic-H). Anal. Calcd for $C_{11}H_{12}O_6$: C, 55.00; H, 5.00. Found: C, 54.93; H, 5.05.

1,2-Bis(methoxycarbonyl)cyclopentadiene (1,2-Cp-2). (a) Methyl chloroformate (18.8 g, 0.2 mol) was added dropwise during 30 min into a stirred solution of cyclopentadienylsodium in THF (100 mL, 0.2 mol) under dry argon at 0 °C, stirring was continued for 1 h, the solvent was removed in vacuo, the residue was extracted with ether (10 × 20 mL), and the ether was evaporated, leaving what seems a mixture of the dimers of 1,2- and 1,3-bis(methoxycarbonyl)cyclopentadiene[25] which was not investigated further. The remainder from the ether extraction was filtered and dried, giving a red solid (18.3 g), which after extraction (Soxhlet) with EtOAc for 16 h left behind NaCl (8 g). The solvent was evaporated at reduced

(28) Frey, J.; Rappoport, Z. *J. Org. Chem.* **1997**, *62*, 8372.

pressure, and the red solid formed was extracted (Soxhlet) with $CHCl_3$ for two weeks. Evaporation of the solvent left a 6:1 mixture of sodium 1,2- and 1,3-bis(methoxycarbonyl)cyclopentadienes (9 g). ^{1}H NMR (D_2O) [1,2-: δ 3.83 (3H, s), 6.06 (1H, t, J = 3.6 Hz), 6.87 (2H, d, J = 3.6 Hz); 1,3-: δ 3.85 (3H, s), 6.58 (2H, d, J = 2.2 Hz), 7.28 (1H, t, J = 2.2 Hz)]. TLC and column chromatography failed to separate the isomers. When a methanolic solution of the mixture was evaporated slowly, a few red crystals of a 93:7 1,2- to 1,3-salts mixture were separated.

(b) A similar reaction mixture was stirred for 1 h at 0 °C, and stirring was continued for 24 h at room temperature. The solvent was evaporated, the red residue was extracted with ether (10 × 30 mL), and the insoluble residue was extracted (Soxhlet) with EtOAc for 2 days. Evaporation of the solvent gave a 9:1 mixture of the sodium salts of 1,2-bis- and 1,2,4-tris(methoxycarbonyl)cyclopentadiene as a red solid. ^{1}H NMR (D_2O) δ: 1,2-: 3.75 (6H, s, MeO), 5.98 (1H, t, H-4), 6.79 (2H, d, H3, H5); 1.2.4-: 3.79 (9H, 3MeO), 7.22 (2H, s, H2, H4). The pure sodium salt of **Cp-3** was isolated by preparative TLC.

(c) With a 2:1 relative molar ratio of methyl chloroformate to sodium cyclopentadienide only the 1,2- and 1,2,4-sodium salts were formed in a ratio of 4:1.

Protonation of 1,2-Bis(methoxycarbonyl)cyclopentadiene Sodium. (a) The 1,2-sodium salt (+7% of the 1,3-salt) was dissolved in water (4 mL), CCl_4 (1.5 mL) was added, and the mixture was stirred with dropwise addition of concentrated HCl (0.5 mL). The organic layer was quickly separated and dried ($MgSO_4$), the salts were filtered, and the ^{1}H NMR spectrum showed that the enol of the 1,2-diester consisted 10% of the mixture. A similar experiment at 330 K showed 5% of the enol of the 1,2-diester.

(b) When the mixture of the sodium salts of the 1,2-di- and the 1,2,4-triesters was likewise protonated and worked up, the ^{1}H NMR spectrum showed that the enol of the 1,2-diester consists 20% of the 1,2-diester mixture.

Exchange Experiments. For exchange of protons, the sample (20 mg) was dissolved in $CDCl_3$ (0.5 mL) and shaken with D_2O (0.15 mL), after which the ^{1}H NMR spectrum was immediately recorded.

Acknowledgment. We are indebted to Dr. Shmuel Cohen for the crystallographic determination and to the Israel Science Foundation for support. Partial support from Cagliari University to G. Cerioni is gratefully acknowledged.

Supporting Information Available: Tables S1−S10 of the details of the crystallographic technique, of bond lengths and angles, and of positional and thermal parameters; stereoviews (Figures S1, S2) of **Cp-4** and **Cp-3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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