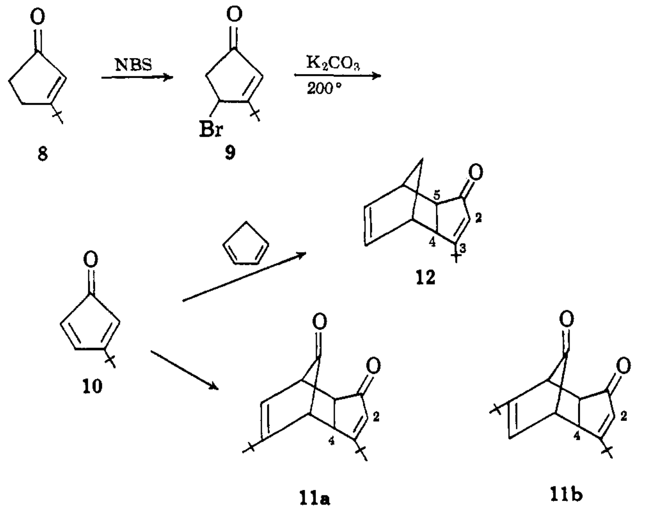
Table I. Spectral Data

		Ultraviolet[a]				Nmr,[b] τ							
Compd	Solvent	λ_{max}, mμ	log ϵ	λ_{max}, mμ	log ϵ	H_2	H_3	H_4	H_5	t-Bu	Other	$\nu_{C=O}$, cm^{-1} [b]	k, l. mole^{-1} sec^{-1} (dimerization)
4	EtOH	217	3.87	395	2.36		3.50		5.07	8.83	$J_{3,5}$ = 1.7 Hz	1708	2.4 × 10^{-5} (25°)
	i-C_8H_{18}	210[c]	3.86	390	2.43								
	Vapor	209	...	385	...								
5a[d]	MeOH[e]	203	3.88	231	3.80		3.35 (W_H = 1.1)		7.12 (W_H = 1.5)		τ 4.13 (doublet)	1700	
	i-C_8H_{18}[f]	193	4.12	226	3.80						τ 6.88 (doublet)	1765	
6a[d]						...	3.30[g]	...	...			1695[g]	
7[d]												1765[g]	
10	MeOH[h]	210	i	375	i								10^2 (−20°)
	i-C_8H_{18}[h]	200	4.71	*Ca.* 380	>1.9								
11[d]	MeOH[j]	202	3.94	231	4.04	4.00	...	...	...	8.78	$J_{2,4}$ = 1.0 H_2	1710	
	i-C_8H_{18}[k]	197	4.14	223	4.00					9.00		1790	
12[d]	MeOH[l]	201	3.73	233	4.07	4.37	...	6.62	7.28	8.82	$J_{2,4} \sim 1$ H_2	1698	
	i-C_8H_{18}[m]	193	3.88	225	4.02								

[a] λ_{max} values reliable to ±3 mμ due to broadness of bands. [b] In CCl_4. [c] Broad band <195 to 220 mμ. [d] The adducts are presumed to be *endo*. [e] $\lambda_{max}^{n \rightarrow \pi^*}$ 334 mμ (log ϵ 1.96). [f] $\lambda_{max}^{n \rightarrow \pi^*}$ 337 mμ (log ϵ 1.91). [g] Taken of a 1:1 mixture of **6** and **7**. [h] At −60. [i] **10** dimerizes more rapidly in methanol than in i-C_8H_{18} and an estimation of ϵ values was not possible. [j] $\lambda_{max}^{n \rightarrow \pi^*}$ 312 mμ (log ϵ 1.89). [k] $\lambda_{max}^{n \rightarrow \pi^*}$ 343 mμ (log ϵ 1.71). [l] $\lambda_{max}^{n \rightarrow \pi^*}$ 309 mμ (log ϵ 1.81). [m] $\lambda_{max}^{n \rightarrow \pi^*}$ 331 mμ (log ϵ 1.64).



cm^{-1} (C=C); $\tau(CCl_4)$ 8.65 (t-Bu), 3.88 (H_2), 4.80 (H_4), 6.50 (H_{5a}), 7.42 (H_{5b}); J = 19.3 (5a,5b), 5.5 (4,5a), and 2.0 hertz (4,5b); H_2 is a singlet. Nitrogen (7 ml/min, STP) was passed through **9** (held at 65°) and then through a vertical potassium carbonate bed (20–40 mesh) maintained at 200°. The system pressure was 1–2 mm and the optimum delivery rate of **9** is about 20 mg/hr. The effluent was passed into a collection tube immersed in liquid nitrogen. Yellow **10** deposited on the walls of the tube. Injection of cyclopentadiene into the tube after stopping the nitrogen flow, followed by warming to ambient temperature, led to a rapid decolorization and production of *ca.* 50% **11** and 50% **12**. Both **11** and **12** were synthesized from the ethylene ketal of **10** obtained by a sequence of reactions that will be described in our complete report. Crude **11** appears essentially homogeneous; however, a distinction between **11a** and **11b** has not yet been made. The minimum percentage of **10** initially collected was determined to be 92% by directing the effluent of a pyrolysis run onto 50 ml of stirred cyclopentadiene for 2.5 hr at −80° and analyzing the product for **11** and **12**. Numerous attempts to obtain crude nmr data for **10** by collecting it at the orifice of an nmr tube at −196°, washing the sample into the tube with a jet of $CDCl_3$–CCl_4 (1:1), and instantly freezing, then warming the sample rapidly to −80°, and rapidly scanning (both absorption and integral modes in separate experiments) the τ 1–5 region at −75° gave only the spectrum of **11** (operation time at −75 to −80° < 30 sec). For the ultraviolet spectra of **10**: (a) **10** was collected in solvent (stirred) at −80° for 5–15 min (giving a 10^{-4} to 10^{-5} *M* solution) followed by rapid transfer to a precooled cell in the spectrometer held at −60°. At *ca.* 10^{-5} *M* **10** in isooctane, there was no change in absorbance of the 200-mμ band during 15 min. Consequently, the minimum initial amounts of **10**:**11** were *ca.* 11.5:1. (b) **10** was collected at −196° for *ca.* 1 hr, followed by addition of solvent (to give approximately a 10^{-3} *M* solution) and transfer to the spectrometer, as above. The 390-mμ band was scanned repeatedly; however, the relatively rapid dimerization at this concentration and temperature precluded our obtaining reliable extinction coefficients.

Table I summarizes the spectral data for **10**–**12** together with rate constants for self-dimerization of **4** and **10**. Some of these data are discussed in the following note.[4]

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Edgar W. Garbisch, Jr.,[5] Richard F. Sprecher[6]

(5) Alfred P. Sloan Foundation Research Fellow.

(6) National Science Foundation Graduate Trainee, 1965–1966.

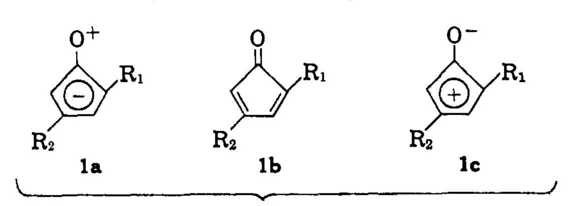
Department of Chemistry, The University of Minnesota
Minneapolis, Minnesota 55455

Received March 21, 1966

On the Origin of the Cyclopentadienone Reactivity

Sir:

The origin of the exceptional reactivity of cyclopentadienone (**1**) to undergo the Diels–Alder dimerization is not known. There have been, however, numerous speculations on this matter. The ones most frequently encountered, perhaps because of their being intuitively attractive and reasonable *a posteriori*, are: (a) **1c** may be uniquely unstable and may not contribute significantly to **1**, thereby increasing the ground-state energy of **1** relative to nonfive-membered ring analogs.[1] (b) **1c** may contribute largely to **1**, thereby increasing the reactivity of **1**, particularly as a dienophile, toward Diels–Alder reaction.[2] This increased reactivity, then, is correlated primarily with a reduction of the free energy of the activated complex structure relative to those of nonfive-membered ring analogs. (c) Ground-state **1** may be a triplet.[3] Of course, the origin of the reactivity of **1** may be of a nature that is difficult to describe in classical terms.[4a] Finally, it may be supposed, on the basis of the relatively high stability of the hydrazone of **1**,[4b] that increasing the contribution of **1a** to **1** would lead to decreasing the reactivity of **1**.



1a **1b** **1c**

1, $R_1 = R_2 = H$ **4**, $R_1 = R_2 = t\text{-Bu}$ **10**, $R_1 = H, R_2 = t\text{-Bu}$

In the preceding note[5] we described the synthesis of 2,4-di-*t*-butyl- and 3-*t*-butylcyclopentadienone, **4** and **10**, respectively, and summarized their spectral properties and rate constants for self-dimerization (Table I in ref 5. We wish to discuss these tabulated data here in connection with the origin of the reactivity of **1**.

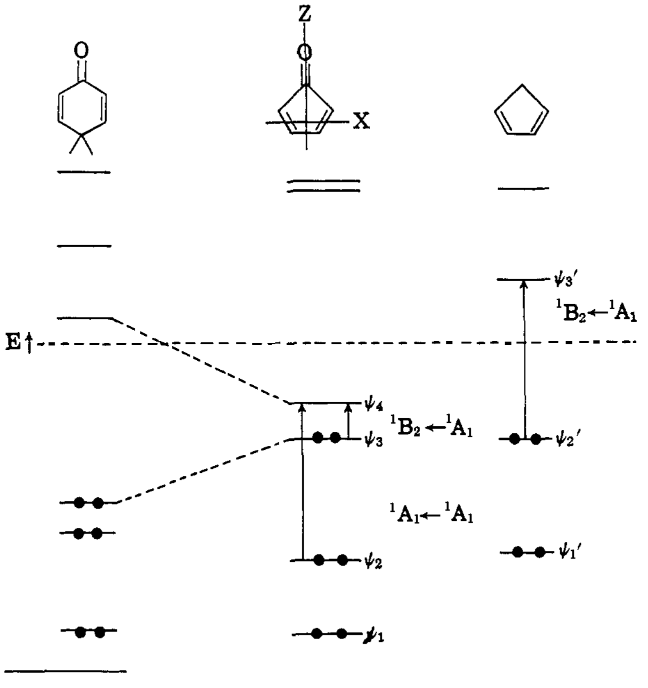
At −20° **10** undergoes the self-Diels–Alder reaction approximately *ten million* (10^7) times faster than does **4** at 25°. Both **4** and **10** are singlet ground-state molecules as evidenced by the determination of the nmr spectrum of **4**, their similar ultraviolet spectra, and the absence of a triplet epr for **10** in methanol matrix at −196°.[6] The similarity between the ultraviolet spectra of **4** and **10**[7] indicates to us that there is no significant perturbation of either π-electronic system and that their spectral properties may be closely representative of those of **1**. We conclude, in addition, that the large decreased reactivity of **4** relative to **10** toward self-Diels–Alder reaction derives almost exclusively from steric retardation. Consequently, the rate of dimerization of **1** may approach that for diffusion control ($k_D \approx 10^{10}$ l. mole^{-1} sec^{-1}).

The H_3 and H_5 magnetic resonances of **4** appear to be unexpectedly high. In order to get approximate expectation chemical shifts for these hydrogens in the absence of contribution from back-polarization (*e.g.*, **1a**) the vinyl hydrogen chemical shift change upon going from cyclopentene to cyclopentadiene was applied to 2,4-di-*t*-butylcyclopent-2-enone (for H_3 of **4**) and 3,5-di-*t*-butylcyclopent-2-enone (for H_5 of **4**). The expected τ values for H_3 and H_5 of **4** are 1.91 and 3.30 ppm, respectively. These are to be compared with the experimental values of 3.50 and 5.07 ppm, respectively. These experimental τ values are *1.6 and 1.8 ppm higher* than expected. It appears likely, consequently, that **1** derives significant ground-state stabilization by contributions from **1a**. We might also mention that the H_3,H_5 coupling of 1.7 hertz (for **4**) is the same as that observed in the ethylene ketal of **10** and in structures bearing similar hydrogen stereorelationships.[8] This is in accord with the idea that these couplings are dominated by σ-bond contributions[8] and, in turn, suggests that the σ-electron framework of **1** is unexceptional.

The carbonyl stretching frequency of **4** is 1708 cm^{-1} and is comparable with those found in cyclopent-2-enones. The six-, seven-, and eight-membered-ring cross-conjugated dienones exhibit carbonyl absorptions at 15–24-cm^{-1} lower wavenumber than those of the corresponding cyclic enones.[9] The significance of this infrared parameter for **4** is questionable as the effects arising from the neighboring *t*-butyl group are at this time undeterminable.

The ultraviolet spectra of **4** and **10** are at first glance similar to those of simple cyclic enones and cross-conjugated dienones except that the high-energy absorptions ($\pi \rightarrow \pi^*$) are at lower wavelengths and the low-energy absorptions (normally $n \rightarrow \pi^*$) are at higher wavelengths than might have been expected. The high-energy band exhibits a solvent dependence that is typical of cyclic enone and cross-conjugated dienone $\pi \rightarrow \pi^*$ transitions. The low-energy bands are essentially solvent independent or, for **4**, may increase slightly in energy upon going from ethanol → isooctane → vapor. This is atypical of $n \rightarrow \pi^*$ transitions which generally exhibit distinctly opposite solvent shifts. Referring to the HMO π-energy diagram (Scheme I)[10a] the

Scheme I



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(1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 272.

(2) C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964).

(3) M. E. Dyatkina, *Zh. Fiz. Khim.*, **22**, 549 (1948).

(4) (a) R. D. Brown, *J. Chem. Soc.*, 2670 (1951); J. Deschamps, *Compt. Rend.*, **246**, 2622, 3065 (1958); (b) K. Hafner, F. Schulz, and K. Wagner, *Ann. Chem.*, **678**, 39(1964).

(5) E. W. Garbisch, Jr., and R. F. Sprecher, *J. Am. Chem. Soc.*, **88**, 3433 (1966).

(6) We wish to thank Charlotte Somers for running the epr spectrum.

(7) Although the ϵ_{max} (λ 200 mμ) for **10** is greater than that for **4**, the absorption band of **10** is considerably narrower than that for **4**.

(8) E. W. Garbisch, Jr., *Chem. Ind.* (London), **41**, 1715 (1964).

(9) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965).

(10) (a) The parameters used are $\alpha_O = \alpha + 2\beta$ and $\beta_{C-O} = \beta_{C-C}$. (b) M. J. S. Dewar in "The Application of Wave Mechanical Methods to the Study of Molecular Properties," R. Daudel, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 66; K. Fukui in "Molecular Orbitals in Chemistry, Physics, and Biology," P. Lowdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p 513.

ground → $\psi_1{}^2\psi_2{}^2\psi_3{}^1\psi_4{}^*$ transition for 4,4-dimethylcyclohexa-2,5-dienone (224 mμ) is expected to appear at higher energies relative to this transition for cyclopentadienone. We assign, therefore, the 385–395-mμ bands of **4** and **10** to ground → $\psi_1{}^2\psi_2{}^2\psi_3{}^1\psi_4{}^*$ ($^1B_2 \leftarrow {}^1A_1$; *x* axis polarized) and the 200–217-mμ band of **4** and **10** to ground → $\psi_1{}^2\psi_2{}^1\psi_3{}^2\psi_4{}^*$ ($^1A_1 \leftarrow {}^1A_1$; *z* axis polarized) transitions. This assignment is substantiated by relative transition intensities. For example, the relative oscillator strengths of the $^1B_2 \leftarrow {}^1A_1$ transitions of **4** and cyclopentadiene (CP) may be compared according to $f_{CP}/f_4 = (\lambda_4/\lambda_{CP})(Q_{CP}/Q_4)$ where Q_{CP} and Q_4 are calculated transition moments and λ_4 and λ_{CP} are experimental wavelengths for the transitions under discussion. We qualitatively take $f_{CP}/f_4 \cong \epsilon_{CP}/\epsilon_4$ and estimate log $\epsilon_4 \simeq 2$, from the known $^1B_2 \leftarrow {}^1A_1$ transition of cyclopentadiene (λ_{CP} 239 mμ (log ε 3.5)). This is to be compared with the observed log ϵ_4, 2.4. Similarly, $\epsilon_4{}^{^1A_1\leftarrow{}^1A_1}/\epsilon_4{}^{^1B_2\leftarrow{}^1A_1}$ was calculated to be approximately 7 × 10, and that observed is approximately 3 × 10.

The ultraviolet spectral data support the qualitative HMO energy diagram shown in Scheme I. *We feel that the dominant origin of the unique reactivity of the cyclopentadienone system lies in the low* $\Delta E_{\psi_3,\psi_4}$ *that exists in* **4** *and* **10**. We adopt the idea of a largely concerted Diels–Alder reaction mechanism. The total π-stabilization energy (δE^π) in the transition state is given by second-order perturbation theory[10a,b] as

$$\delta E^\pi = 2\Big(\sum_i^{\text{occ}} \sum_j^{\text{unocc}} - \sum_i^{\text{unocc}} \sum_j^{\text{occ}}\Big)\frac{(C_{1_i}C_{1_j} + C_{4_i}C_{2_j})^2\beta^2}{E_i - E_j}$$

where C_{1_i} and C_{4_i} represent the coefficients of the AO's on carbons 1 and 4 of the *i*th MO of diene; C_{1_j} and C_{2_j} are the coefficients of AO's on carbons 1 and 2 of the *j*th MO of the dienophile; and β is the resonance integral between the two interacting AO's of both diene and dienophile. For Diels–Alder reactions involving **1**, the dominant terms of the above summation are expected to involve only the highest occupied and lowest unoccupied orbitals of diene and dienophile. This follows from the low $\Delta E_{\psi_4,\psi_3}$ relative to the other ΔE's of **1**. With this approximation, the above equation simplifies to

$$\delta E^\pi = \left[\frac{(C_{1_I}{}^{\text{occ}}C_{1_J}{}^{\text{unocc}} + C_{4_I}{}^{\text{occ}}C_{2_J}{}^{\text{unocc}})^2}{E_I{}^{\text{occ}} - E_J{}^{\text{unocc}}} - \frac{(C_{1_I}{}^{\text{unocc}}C_{1_J}{}^{\text{occ}} + C_{4_I}{}^{\text{unocc}}C_{2_J}{}^{\text{occ}})^2}{E_I{}^{\text{unocc}} - E_J{}^{\text{occ}}}\right]2\beta^2$$

where subscripts I and J refer to diene and dienophile, respectively. The occupied and unoccupied orbital wave function symmetries will govern largely the magnitude of the numerator terms (through relative signs of coefficients) of the above equation and lead to the correct prediction of the carbon atoms involved in bonding during the Diels–Alder reaction. The high Diels–Alder reactivity of **1** relative to those for most other diene–dienophile pairs is qualitatively understood in terms of the above discussion. We note also that ψ_2' of cyclopentadiene and ψ_3 of **1** (see Scheme I) are degenerate due to their equivalent symmetries (antisymmetric); however, this degeneracy is expected to be relieved somewhat in higher order approximations. Nevertheless, it is clear that cyclopentadiene will be a most suitable substrate for trapping the highly reactive **1**. Application of the above equation leads to the expectation that the cross-dimerization of cyclopentadiene and **1** is expected to occur somewhat less readily than dimerization of **1** and more readily than dimerization of cyclopentadiene. This appears to have been borne out experimentally. Also in agreement with experiment, the above PMO treatment leads to the prediction that **1** will react with cyclopentadiene most favorably as a dienophile and more readily than it will react with maleic anhydride as a diene.

Apropos to the origin of the reactivity of **1** toward Diels–Alder dimerization are the interesting observations of Eaton and Hudson[11] that the ethyl and ethylene ketals of **1** self-dimerize 5 × 10^2 and 5 × 10^5 times more rapidly than does cyclopentadiene. The low-energy $^1B_2 \leftarrow {}^1A_1$ transitions appear at 239, 270, and 280 mμ for cyclopentadiene and the ethyl and ethylene ketals of **1**, respectively. Although ε values could not be obtained for these ketals of **1**,[11] we have determined them for the methyl and ethylene ketals of **10** and found them to be of comparable magnitude to that for cyclopentadiene ($\lambda^{\pi\rightarrow\pi^*}$ (i-C_8H_{18}) 270 and 280 mμ and log ε 3.09 and 3.04, respectively[12]). We feel that the ketal transitions probably are correctly characterized.[12] Perturbation (second-order) interaction between the nonbonded electron-pair orbitals (sp^3) on oxygen and the MO's (at carbons 1 and 4) of the diene system of these ketals is calculated to reduce the energy separation between both the lowest and highest occupied and lowest unoccupied MO's. The increasing reactivity toward dimerization with increasing $\lambda^{\pi\rightarrow\pi^*}$ of the above systems appears to be in accord with expectation from the PMO approach described above.[13]

Finally, we wish to draw attention to the closely similar ultraviolet spectra of thiophene 1,1-dioxide[14] and of the ethylene ketal of **10**, and suggest that the high reactivity of this sulfone toward Diels–Alder dimerization[14] may be conveniently understood in terms of second-order perturbation theory.

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Edgar W. Garbisch, Jr.,[15] Richard F. Sprecher[16]
Department of Chemistry, The University of Minnesota
Minneapolis, Minnesota 55455

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[11] P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965).

[12] These λ_{max} values are unchanged in methanol. Also we see the high energy π → π* transitions, as expected. For the dimethyl and ethylene ketals of **10**, these absorptions appear at 195 (log ε 3.34) and 196 (log ε 3.35) in isooctane and 203 (log ε 3.11) and 203 mμ (log ε 3.14) in methanol, respectively. Low intensity (ε < 100) transitions are observed at *ca.* 225 and 235 mμ for the dimethyl and ethylene ketals (in isooctane), respectively. These bands appear to experience a hypsochromic shift in methanol.

[13] The higher energy $^1B_2 \leftarrow {}^1A_1$ transition of the dimethyl ketal relative to the ethylene ketal of **10** presumably is due to a reduction in interaction between the oxygen lone pairs and the diene π-system in the dimethyl ketal (due to rotation about the C–O bonds of $\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}}$ induced by methyl group repulsions) relative to the ethylene ketal (where such rotations are restricted).

[14] W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, **76**, 1932 (1954).

[15] A. P. Sloan Foundation Research Fellow.

[16] National Science Foundation Graduate Trainee, 1965–1966.