t-Butyl-Substituted Cyclopentadienones[1]

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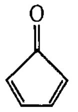
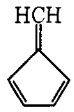
Abstract: Monomeric 3-*t*-butyl- and 2,4-di-*t*-butylcyclopentadienones (**3** and **18**) have been isolated. Their ultraviolet spectra are similar to that of fulvene and probably correspond closely to that of cyclopentadienone. The unusually high field chemical shifts of τ 5.07 and 3.50 for the α and β protons of **18** are thought to reflect largely an increased π-electron density at the respective olefinic carbon atoms relative to those in cyclopentenone. The isolation of monomeric 2-*t*-butylcyclopentadienone (**26**) was not successful because of the pronounced reactivity of **26** toward dimerization. Diels–Alder dimerizations of **18**, **3**, and **26** occur stereoselectively with the formation of *endo* dimers and with relative rates of 1, 5×10^6, and $>10^8$. The stereochemical courses and relative rates of these dimerizations appear to be controlled mainly by nonbonded steric effects. A rate constant of $10^8\ M^{-1}\ \mathrm{sec}^{-1}$ for the dimerization of cyclopentadienone at 30°, which approaches that of about $10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ for diffusion control, was estimated from a combination of second-order perturbation and electrostatic interaction theories and experimental rate constants for dimerizations of several five-membered ring dienes and dienophiles. The small energy gap between the highest occupied and lowest unoccupied π-MO's of cyclopentadienone is thought to be mainly responsible for the large magnitude of this estimated rate constant. Rates of dimerizations of several derivatives of cyclopentadiene were estimated and a qualitative explanation was given for the unusually high reactivity of the ethylene ketal of cyclopentadiene toward dimerization.

Cyclopentadienone dimerizes in the Diels–Alder way with such pronounced facility that all attempts toward its isolation or direct detection as a monomer have failed.[2] Its existence as a metastable monomer has been demonstrated indirectly, however, by trapping experiments.[2] Probably the most meaningful testimony to the reactivity of cyclopentadienone is that, with the exception of indenone and a probable di-*t*-butylcyclopentadienone,[3] only tri- and tetrasubstituted derivatives containing at least two phenyl groups have been isolated as monomers.[4]





Fulvene is in remarkable contrast to cyclopentadienone in its reactivity toward Diels–Alder dimerization. Although it polymerizes readily in the neat state, it can be distilled and is stable in dilute solution.[5] The physical basis of this exceptional reactivity of cyclopentadienone must correlate with the electronic changes that occur upon going from fulvene to cyclopentadienone, and these largely result from increasing the electronegativity of one atom. Both fulvene and cyclopentadienone have C_{2v} symmetry and their *exo*-trigonal atoms lie along their symmetry axes. The dominant effect of exchanging an oxygen atom for the *exo*-carbon atom of fulvene, therefore, will be to lower in energy the electronic states that are symmetric with respect to the vertical molecular plane of symmetry, and to leave unperturbed those states that are antisymmetric. With regard to the π states, as we will discuss later, this leads to a decrease in the energy separation between the highest occupied and lowest unoccupied molecular orbitals. It is unlikely that the effect of oxygen is such as to reduce this energy separation to a value sufficient to produce a ground-state triplet cyclopentadienone. However, this idea has been suggested as a possible explanation for the cyclopentadienone reactivity.[2,6]

Before considering the origin of the cyclopentadienone reactivity further, we felt it important to obtain spectral data on minimally substituted cyclopentadienones and from them determine experimentally whether or not any exceptional electronic features exist. As the probability of successfully obtaining such data on monomeric cyclopentadienone was from all indications negligible, it was decided to attempt the syntheses of several *t*-butyl-substituted cyclopentadienones. Our hope was that the *t*-butyl groups would (1) sterically retard the dimerization process to the extent that spectral data on the monomers could be obtained and (2) minimally perturb the cyclopentadienone fragment from that of the parent system.

I. Synthesis[7]

Synthesis of 3-*t*-Butylcyclopentadienone (3). Initial attempts were made to synthesize **3** by acid-catalyzed hydrolysis of its ethylene ketal (**8**). This approach was abandoned as only the dienone dimer, **4**, was produced and it became evident that the reactivity of **3** toward dimerization was too great to allow its isolation as a monomer under accessible hydrolysis and isolation conditions (Scheme I).

An alternative approach involving dehydrobromination of **2** to produce **3** was successful. Bromination of **1** following DePuy's procedure[2] produced **2**. The absence of any observable coupling between the methylene

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[1] For a preliminary account of this work, see E. W. Garbisch, Jr., and R. F. Sprecher, *J. Amer. Chem. Soc.*, **88**, 3433, 3434 (1966).

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

[3] U. Krüerke and W. Hübel, *Chem. Ber.*, **94**, 2829 (1961).

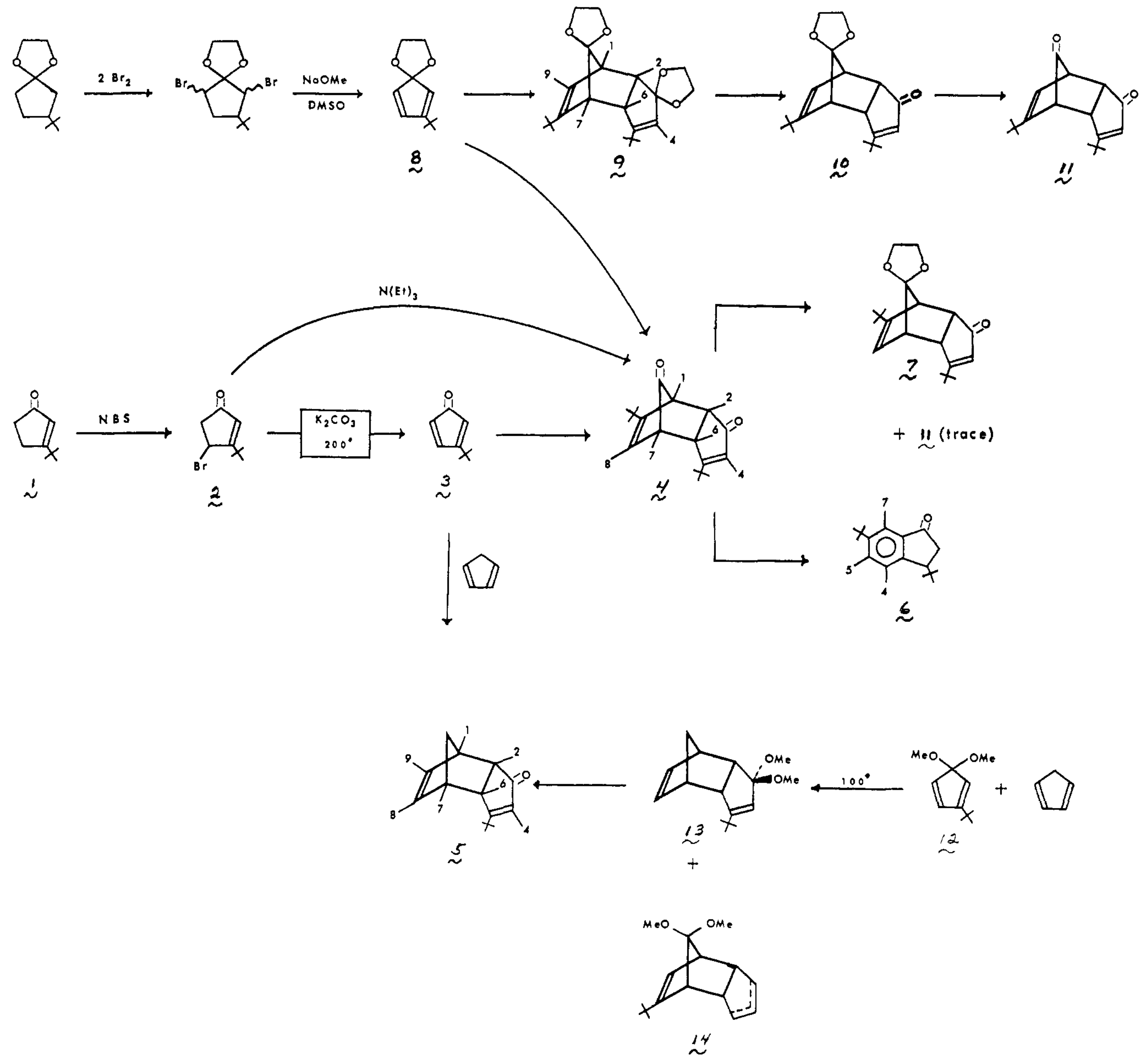
[4] M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

[5] (a) J. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr.*, 177 (1956); 1066 (1960); (b) D. Meuche, M. Neuenschwander, H. Schaltegger, and H. U. Schlunegger, *Helv. Chem. Acta.*, **47**, 1211 (1964); (c) H. Schaltegger, M. Neuenschwander, and D. Meuche, *ibid.*, **48**, 955 (1965).

[6] M. E. Dyathkina, *Zh. Fiz. Khim.*, **22**, 549 (1948).

[7] Spectral (ir, uv, and nmr) data on the isolated molecules discussed in this section are collected in Tables V and VI in the Experimental Section. These data will be discussed in connection with structure identification only in instances where they appear not to be self-explanatory.

Scheme I



and vinyl protons,[7] together with the observation of facile dehydrobromination of triethylamine[8] to give ~96% **4** and ~4% **11**, may be construed as evidence that the bromine atom resides on C_4 rather than C_5. The production of **3** was accomplished by passing a mixture of **2** and nitrogen through a column of hot potassium carbonate. 3-*t*-Butylcyclopentadienone (**3**) was condensed as a bright yellow material on a glass surface cooled in liquid nitrogen. Upon warming to ambient temperature, the yellow color disappeared and the Diels–Alder dimer, **4**, was isolated. Directing the nitrogen stream from the carbonate column onto cyclopentadiene at −80° produced a mixture of 92% **5** and 8% **4**. Apparently **4** was produced by dimerization of **3** on the column, for when **3** was collected in isooctane, rather then cyclopentadiene, no change in the uv spectrum of the solution could be detected over a period of 15 min at −60°.

Spectral data[7] are consistent with the structure of **4** being that shown, except that they do not establish whether a *t*-butyl group resides at C_8 or C_9. The ir spectrum of **4** shows the expected absorptions at 1790, 1710, and 1600 cm^{-1} due to the carbonyl groups at C_{10} and C_3, and the conjugated double bond, respectively. Its uv spectrum in isooctane shows absorptions centered at 197, 223, and 329 mμ (log ϵ = 4.14, 4.00, and 1.77) due to the norbornene double bond ($\pi \rightarrow \pi^*$), the conjugated ketone system ($\pi \rightarrow \pi^*$), and a carbonyl group ($n \rightarrow \pi^*$), respectively. The band at 329 mμ shifted to 312 mμ in methanol as expected for a $n \rightarrow \pi^*$ transition. The nmr spectrum of **4** shows resonances arising from two vinyl protons, four allylic protons, and two vinyl *t*-butyl groups. The vinyl proton resonances at τ 4.24 appear as four absorptions that give first-order coupling constants of 3.9 and 1.7 cps, while those at τ 4.00 appear as a doublet (J = 1.0 cps). The couplings correspond to those expected for H_8 (or H_9) and H_4, respectively. Absorptions for three of the four allylic protons were grouped together between τ 6.38 and 6.92 and precluded detailed analysis, while those for the fourth were seen at τ 7.20 as a four-line multiplet exhibiting first-order

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(8) 5-Bromocyclopent-2-enone is unreactive toward triethylamine.[2]

couplings of 7 and 5 cps. Since neither of these couplings correspond to those of the vinyl protons, and H_4 is expected to couple to H_6 but not to H_2,[2] the resonances centered at τ 7.20 were assigned to H_2. The two couplings to H_2 then would be due to H_1 and H_6 and would indicate an *endo* configuration for the dimer.[9]

The vinyl *t*-butyl group in the norbornene ring of **4** is thought to be on C_9 from the results of the following experiments. Pyrolysis[2] of **4**, followed by mild acid catalyzed isomerization of the product, which appeared[10] to be 3,6-di-*t*-butyl-3a,7a-dihydroindanone, led to **6**. The infrared spectrum of **6** showed an absorption at 1705 cm^{-1} as expected of a conjugated ketone. The aromatic proton magnetic resonances were not analyzable; however, the low-field resonances centered at τ 2.35 (1 H) were assigned to the aromatic proton *ortho* to the detone substituent by analogy with other aromatic ketones.[11] When these resonances were irradiated with a field strength of 0.7 mG, the high-field aromatic proton resonances (2 H) simplified to an AB spectrum having J_{AB} = 8.0 cps. The magnitude of this coupling is compatible only with that expected for *ortho* protons.[12] Consequently, the *t*-butyl group in **6** must be on C_6 and that in the norbornene ring of **4** must be on C_9.

Dienone dimer **11**, which was detected (not isolated) as the minor product (*ca.* 4%) of the Diels–Alder dimerization of **3**, was obtained by acid-catalyzed hydrolysis of the ketal groups in **9**. Dimer **9** was obtained as the only detectable product from the dimerization of **8**. The structure of **9** is based upon the results[7] of a least-squares iterative analysis[13] of its nmr spectrum. Proton assignments were made as follows. A doublet (J = 0.2 cps) at τ 4.80 was assigned H_4. The assignment of H_6 was based on the presence of a small coupling (0.2 cps) of the proton at τ 6.61 to H_4 which collapsed when H_4 was irradiated with a radiofrequency field strength of 0.3 mG. The proton at τ 7.29 exhibited a small coupling of 0.4 cps to the vinyl proton at τ 4.21 and substantial couplings of 7.6 and 5.0 cps to H_6 and another proton, respectively. Consequently, it was assigned H_2 and the 5.0 cps coupling must be with H_1. The remaining allylic proton at τ 7.36 is assigned to H_7. Since the vinyl proton at τ 4.21 couples more strongly with H_1 (J = 3.8 cps) than with H_7 (1.6 cps), it is assigned to H_9. Consistent with this assignment is the small coupling between H_9 and H_2 of 0.4 cps, which may be expected to arise in the near-planar zigzag pattern of the $H{-}C_9{-}C_1{-}C_2{-}H$ system.[14] Also found is a coupling of 1.5 cps beteeen the bridgehead protons, which may be compared to a coupling of 1.12 cps found in norbornene.[15] Since H_2 couples substantially to both H_1 and H_6 (see above), the dimer **9** was given the *endo* configuration.[9]

Acid-catalyzed ketal exchange[16] between acetone and **9** led quantitatively to **10** (mp 119–121°).[7] Partial ketalization[17] of **4** gave **7** (mp 94–95°).[7] Hydrolysis of the C_{10} ketal group in **10** in aqueous sulfuric acid gave **11** (mp 124–126°; compare the melting point of **4**, 63–65°).[7] A comparison of the nmr spectra of **4** and **11** showed substantial similarities, the most notable difference being the chemical shifts of H_8 (τ 4.24) and H_9 (τ 3.90), respectively. The minor product of the dimerization of **3** had vinyl proton multiplicities and chemical shifts, together with *t*-butyl chemical shifts that were identical with those of **11** and therefore was assigned that structure.

The structure of **5**, the Diels–Alder dimer of cyclopentadiene and **3**, was assigned on the basis of spectral data.[7] Strong ir absorptions at 1698 and 1590 cm^{-1} together with a uv spectrum compatible only with an α,β-unsaturated ketone,[7] shows that **3** reacted as the dienophile. The nmr spectrum of **5** has resonances attributable to three vinyl protons, one vinyl *t*-butyl group, two aliphatic protons, and four allylic protons.[7] By analogy with the spectra of **4**, **9**, and **11**, the four-line multiplet centered at τ 7.28 was assigned to H_2 (no coupling to vinyl protons was detectable). The presence of two substantial couplings to H_2 (5.9 and 5.0 cps) is indicative of the *endo* configuration. A multiplet centered at τ 6.62 was assigned to H_6 on the basis of apparent couplings of 1.1 cps to H_4 at τ 4.32 and 5.9 cps to H_2. First-order couplings of 5.0 and 4.3 for $J_{1,2}$ and $J_{6,7}$, respectively, were deduced from the remaining splittings in the H_2 and H_6 resonances. An independent synthesis of **5** was achieved through selective hydrolysis of a mixture of **13** and **14** that was obtained from the reaction between **12** and cyclopentadiene. The dimer that underwent facile ketal hydrolysis was assigned **13** and that unaffected under the conditions used was assigned **14**.[18]

Synthesis of 2,4-Di-*t*-butylcyclopentadienone (18). Our synthetic approach was that initially attempted for the preparation of **3**, *i.e.*, synthesis followed by hydrolysis of the ethylene ketal of **18**. However, bromination of a mixture of stereoisomeric **15** in ether did not proceed to give the α,α'-dibromo ketone ethylene ketal as expected.[19] Rather, it led to a mixture of **16** and **17** in which the former predominated.[7] Our understanding of this reaction is obscure. At ambient temperature, **17** was unreactive toward triethylamine. However, dehydrobomination of **16** using triethylamine proceeds rapidly to give **18** which was obtained as a yellow material melting between 30 and 31°. The structure of **18** was established by its conversion to **20** which was synthesized independently from known[20] **19**.

Upon standing at room temperature for 2 days, **18** was converted to a single Diels–Alder dimer as evidenced by its ir and uv spectra.[7] The nmr spectrum[7] of the dimer shows two vinyl proton absorptions, one of which arises from a proton β to the α,β-unsaturated carbonyl and exhibits no coupling to any other proton

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(9) J. C. Davis, Jr., and T. V. Van Auken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965).

(10) The nmr spectrum of the product showed neither aromatic proton nor aliphatic *t*-butyl resonances.

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 258–260; H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(12) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 208 (1965).

(13) The LAOCOON-II program provided by Dr. A. A. Bothner-By was used on a CDC 1604. All observable lines were included in the iteration.

(14) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(15) E. W. Garbisch, Jr., *Chem. Commun.*, 332 (1968).

(16) C. Djerassi, "Steroid Reactions," Holden Day, Inc., San Francisco, Calif., 1963, pp 15–22.

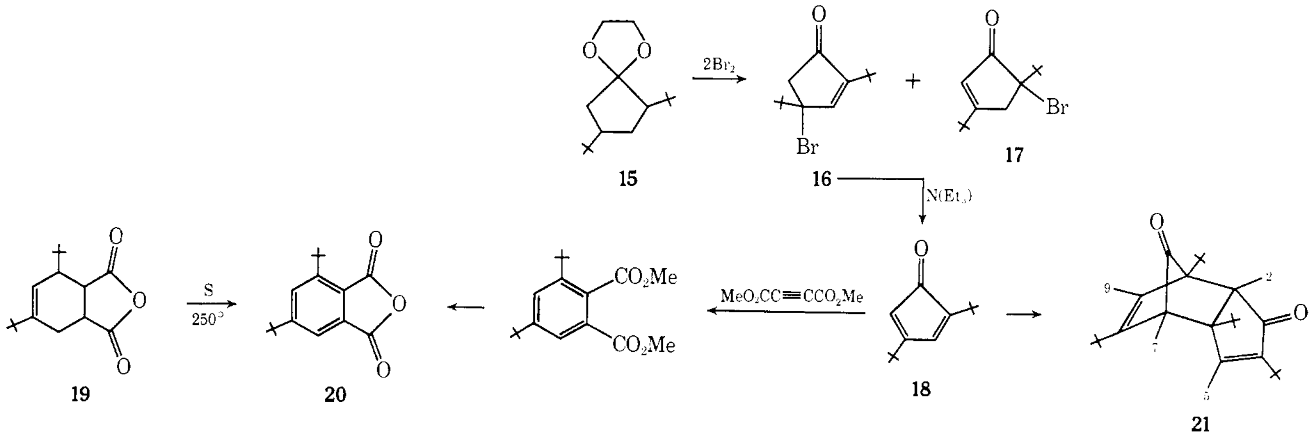
(17) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 309.

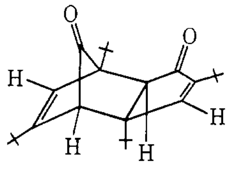
(18) C_8-ketals are more readily hydrolyzed than C_{10}-ketals in this ring system; see Experimental Section for the syntheses of **10** and **11**.

(19) (a) P. E. Eaton and R. A. Hudson, *J. Amer. Chem. Soc.*, **87**, 2769 (1965); (b) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965).

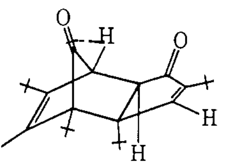
(20) P. D. Bartlett, M. Roha, and R. Stiles, *J. Amer. Chem. Soc.*, **76**, 2349 (1953).

Scheme II





21a

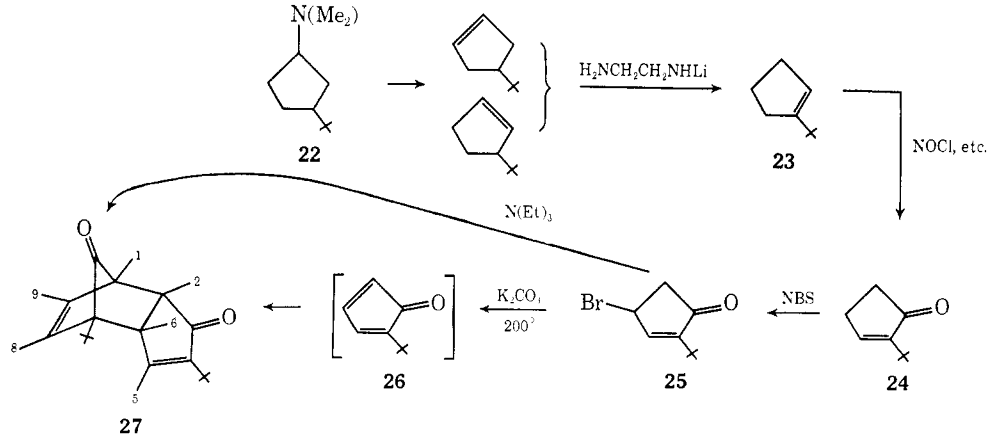


21b

and the second of which exhibits a coupling (J = 1.8 cps) to one of the two remaining allylic hydrogens. As no coupling is observed between the two allylic protons, the structure of the dimer most likely is either **21**, **21a**, or **21b**. We have on the basis of the expected *endo* course for the dimerization of **18**, tentatively chosen dimer **21** as being the correct structure (Scheme II).

Synthesis of 2-*t*-Butylcyclopentadienone (26). After determining rate constants for dimerizations of **3** and **18** and finding that **3** is about ten million times more reactive toward dimerization than **18** (see subsequent section), we wondered whether the low relative reactivity of **18** was due primarily to steric retardation or whether the 2-*t*-butyl group otherwise was reducing its reactivity toward dimerization. We were interested, therefore, to compare the dimerization reactivities of **3** and **26**.

Scheme III



Reductive amination[21] of 3-*t*-butylcyclopentanone gave **22** which was converted to a mixture of 3- and 4-*t*-butylcyclopentenes by a Hoffman elimination. Alkene equilibration using lithium ethylenediamine[22] produced a mixture of *t*-butylcyclopentenes containing 92% **23**. Reaction of **23** with nitrosyl chloride, followed by dehydrochlorination of the adduct with pyridine and then hydrolysis of the resulting α,β-unsaturated oxime with aqueous hydrochloric acid, gave **24** (Scheme III).[7] Bromination of **24** with NBS gave **25**.[7] As the vinyl proton of **25** was found to couple with only one other proton, the bromine atom resides on C_4 rather than C_5.

Pyrolysis of **25** over potassium carbonate, under conditions similar to those used for the generation of **3**, led to collection of a yellow material at −196°. Upon warming, the material decolorized and **27** was isolated. Also, **27** was produced as the only detectable product of the reaction between **25** and triethylamine. Under conditions that produced a 10^{-5} M solution of **3** in isooctane (at −80°) which showed no change in the uv over a period of 15 min, **26** had dimerized completely. Apparently, **26** dimerizes at least an order of magnitude faster than does **3**.

Spectral data[7] for **27** support the structure shown. The nmr spectrum[7] of **27** shows one (τ 3.13) of the three vinyl protons to be located on C_5, *i.e.*, β to the conjugated carbonyl group. This proton is coupled only to one proton, H_6, with $J_{5,6}$ = 2.6 cps. The H_6 resonances were found as a four-line multiplet, centered about τ 6.70, exhibiting first-order couplings of 2.6 and 6.3 cps. A four-line multiplet, arising from one proton, showing splittings of 6.3 and 4.9 cps, was found centered about τ 7.18. These resonances were assigned to H_2 and the 4.9- and 6.3-cps couplings must be to H_1 and H_6, respectively. The presence of two large couplings to H_2

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[21] M. L. Moore, *Org. Reactions*, **5**, 319 (1949).

[22] L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958).

require that a hydrogen be attached to C_1 and that the adduct have the *endo* configuration.[9] A *t*-butyl group must be bonded to C_7, as H_6 is found to couple to H_5 and H_2. The aliphatic region of spectrum resembles closely that reported for the dimer of 2-chlorocyclopentadienone.[2] The structure postulated[2] for this dimer is analogous to that proposed for **27**.

II. Reactivities of the *t*-Butylated Cyclopentadienones toward Dimerization

Second-order rate constants for the dimerizations of **3** at −20° and **18** at 25° were determined by monitoring the reactions in the uv and pmr spectral regions, respectively. The dimerization of **26** was too fast to follow. As mentioned earlier, the rate constant for this dimerization must be at least an order of magnitude greater than that for the dimerization of **3**.

A sample of **3** in isooctane was collected at −80° and then injected into a uv cell which was thermostated at −20°. The solution absorbances at 210 mμ were reported as a function of finite time and after reaction completion; A and A_∞, respectively. A plot of $1/(A - A_\infty)$ *vs.* time was linear, in accordance with

$$1/(A - A_\infty) = kt(\epsilon_m - \epsilon_d/2) + \text{constant}$$

Using ϵ_m and ϵ_d, the experimental extinction coefficients at 210 mμ for monomer and dimer, respectively, together with the slope of the best visual line, k was estimated to be $10^2\ M^{-1}\ \text{sec}^{-1}$. As the dimerization of **3** produces about 96% **4** and 4% **11**, the second-order rate constants for the two modes of dimerization are roughly 96 and 4 $M^{-1}\ \text{sec}^{-1}$, respectively.

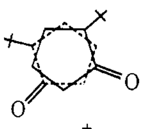
Nmr spectra of the methyl resonances of a 0.24 *M* solution of **18** in carbon tetrachloride were recorded at 25° as a function of time. In agreement with the rate expression

$$[\mathbf{18}]_0/[\mathbf{18}]_t = kt[\mathbf{18}]_0 + 1$$

where the ratios (total areas of methyl resonances)/(areas of methyl resonances of **18**) were taken equal to $[\mathbf{18}]_0/[\mathbf{18}]_t$, a plot of $[\mathbf{18}]_0/[\mathbf{18}]_t$ *vs.* time was linear. From the slope of the line and the initial concentration of **18**, k was estimated to be $2 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$.

The Diels–Alder dimerizations of **3**, **18**, **26**, and **9** occur with remarkably high degrees of stereoselectivity, considering that eight modes (four *exo* and four *endo*) of addition are possible for each. Expecting **3**, which dimerizes to give about 4% of a second *endo* adduct, and **18**, whose dimer configuration is unknown, each dimerization produced only one detectable adduct and that has the *endo* configuration. The generally large kinetic preference for *endo* Diels–Alder dimerizations apparently derives largely from electronic factors that are bonding in origin.[23] Nonbonded interactions such as electrostatic ones that arise between dipoles may favor either *exo* or *endo* addition.[24] For cyclopentadienone, as we shall discuss later, electrostatic interactions are expected to stabilize *endo* addition by about 3.3 kcal/mole and destabilize *exo* addition by a comparable amount. Considering the usual dominance of *endo* additions in the absence of dipolar and severe steric effects,[23,25] nonbonded steric interactions that are greater by as much as 10 kcal/mole in the *endo* than the *exo* mode transition states may be required before *exo*-cyclopentadienone adducts become detectable. Consequently, our presumption that **21** has the *endo* configuration seems reasonable; however, this matter must be reconciled.

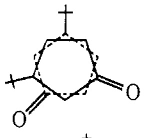
The observed modes and relative reactivities of *endo* dimerizations of **3**, **18**, and **26** appear to be governed largely by nonbonded steric effects. Of the four possible *endo* modes for each dimerization, the favored ones may be predicted correctly by selection of the transition state structures that appear to be least prohibitive sterically. Shown below are qualitative top-view projections of these transition states that lead to **21**, **11**, **4**, and **27**, namely, **21**‡, **11**‡, **4**‡, and **27**‡, respectively. Beneath each projection are listed the nonbonded interactions involving the *t*-butyl groups together with the second-order rate constants for the dimerizations (in $M^{-1}\ \text{sec}^{-1}$). The relative rates clearly vary inversely with the severity of steric interactions. It appears impossible to extrapolate these data to obtain an estimated rate constant for the dimerization of cyclopentadienone. However, we feel confident that this rate constant must be greater than that for the dimerization of **26**; *i.e.*, it will be $\gg 10^3\ M^{-1}\ \text{sec}^{-1}$ at −60° and may approach the diffusion control limit of about $10^{10}\ M^{-1}\ \text{sec}^{-1}$. It is not surprising, then, that we obtained no positive indication (*e.g.*, deposition of yellow material at −196°) for a successful generation and collection of cyclopentadienone under conditions that led to the collection of **3** and apparently **26**.



27‡

4 Bu,H

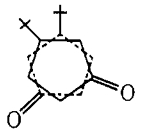
$k_{-60°} > 10^3$



4‡

1 Bu,O
3 Bu,H

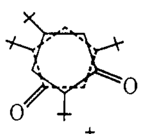
$k_{-20°} \approx 10^2$



11‡

1 Bu,Bu
2 Bu,H

$k_{-20°} \approx 4$



21‡

1 Bu,Bu
2 Bu,O
4 Bu,H

$k_{25°} = 2 \times 10^{-5}$

Comment regarding the stereochemical course of the dimerization of **8** is best made here. The stereochemistry of the sole product of this reaction corresponds to that of the minor product, **11**, arising from the dimerization of **3**. Although this result was not anticipated at the time for the experiment, it now can be rationalized in terms of nonbonded steric effects. In the dimerization of **8**, the nonbonded steric repulsions are reversed from those for the two observed modes of reaction encountered in the dimerization of **3** (consider **4**‡ and **11**‡ with ethylene ketal rather than carbonyl groups). The vicinal ketal–*t*-butyl interaction apparently is greater than that arising from two vicinal *t*-butyl groups, and the dimerization of **8** proceeds to give **9** exclusively.

III. Spectra of 3 and 18

Uv Spectra. The uv spectra of **3** and **18** (see Table VI) each show two absorption bands having maxima around 210 (high extinction) and 385 mμ (low extinction). Because both bands fail to exhibit a blue shift upon changing from hydrocarbon to alcohol solvents,

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[23] W. C. Herndon and L. H. Hall, *Tetrahedron Lett.*, 3095 (1967).

[24] A. Wasserman, "Diels-Alder Reactions," Elsevier Publishing Co., New York, N. Y., 1965, Chapter 5; L. Horner and W. Dürckheimer, *Chem. Ber.*, 95, 1219 (1962).

[25] Note the exclusive production of *endo* adduct **5** from the reaction between **3** and cyclopentadiene. Dipolar effects are minimal in this dimerization.

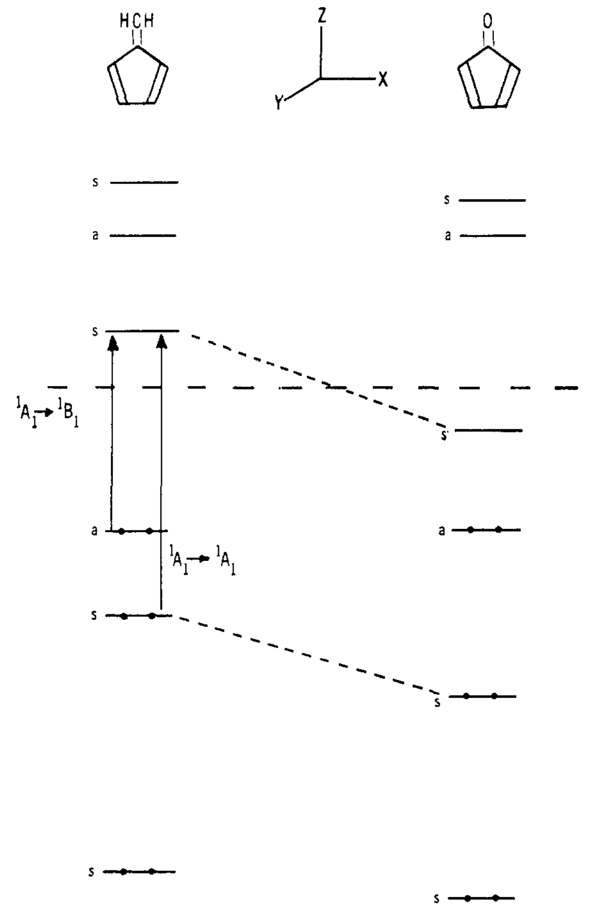

Figure 1. HMO energy diagrams for fulvene and cyclopentadienone.[39]

we have assigned them as arising from $\pi \rightarrow \pi^*$ transitions.[26] The $^1A_1 \rightarrow {}^1A_1$ and $^1A_1 \rightarrow {}^1B_1$ transitions, shown in Figure 1, are polarized, respectively, along the z axis (long and polar axis) and x axis (short and nonpolar axis) and are expected to correlate with high- and low-transition probabilities. Consequently, we have assigned the 210- and 385-mμ absorptions to the $^1A_1 \rightarrow {}^1A_1$ and $^1A_1 \rightarrow {}^1B_1$ transitions, respectively, as shown in Figure 1. The assignments follow, qualitatively, the relative transition energies expected for these transitions. The similarity between the uv spectra of **3** and **18** is empirical evidence that the *t*-butyl groups minimally perturb the cyclopentadienone π system.

The uv spectrum of fulvene in ethanol is similar to those of **3** and **18**. It shows absorption maxima at 241.5 mμ (ϵ 13,900) and 360 (257).[5c] Both SCF[27] and CI[28] calculations support assignments of $^1A_1 \rightarrow {}^1A_1$ and $^1A_1 \rightarrow {}^1B_1$ transitions to the bands at 241.5 and 360 mμ, respectively. As HMO calculations lead to the same assignments, we feel that the spectral assignments made for the cyclopentadienones, **3** and **18**, probably are correct.

We mentioned in the introduction that substitution of an oxygen atom for the methylene group of fulvene should effect an energy lowering of the states symmetric with respect to the vertical molecular plane of symmetry (y–z) and not affect, except for small first-order inductive (coulomb integral) effects, those states antisymmetric with respect to this plane. The result of this substitution would be, then, to decrease the energy gap between the highest occupied and lowest unoccupied MO's in the ground state of cyclopentadienone relative to that in fulvene. This effect is qualitatively reflected in the relative energies of the $^1A_1 \rightarrow {}^1B_1$ transitions for fulvene and cyclopentadienones **3** and **18**.

Nmr Spectrum of 18. The unexpected features of the nmr spectrum of **18** are the unusually high chemical shifts (τ 5.07 (α) and 3.50 (β) ppm) displayed for the two vinyl protons. The vinyl proton coupling of 1.7 cps and the *t*-butyl chemical shifts are unexceptional.

The α- and β-vinyl proton chemical shift changes encountered upon the conversion of cyclopentenone to cyclopentadienone will be governed largely by contributions due to changes in π-electronic charge densities, ring current shieldings, and other magnetic anisotropic shieldings. A qualitative estimate of the contribution due to the last is estimated empirically to be -0.82 ppm (downfield shift) from the vinyl proton chemical shift change upon going from cyclopentene to cyclopentadiene.[29] Adding -0.82 ppm to the vinyl protons of **1** and **24** leads to values for the chemical shifts of the α and β protons of **18** that are expected, provided **18** has no "ring current" and has the same π-charge densities as cyclopentenone (see Table I). Differences between the experimental vinyl proton chemical shifts of **18** and those expected may be regarded as arising from ring current effects and/or from effects of π-electron densities that differ from those of cyclopentenone.

The observed chemical shifts of the α and β protons of **18** both are at about 1.5 ppm higher field than expected. As the *t*-butyl chemical shifts *are the same* for **1**, **18**, and **24**, we conclude that a negligible fraction of the 1.5-ppm vinyl proton shift can be attributed to induced paramagnetic ring currents.[30] For example, the ring current vinyl proton shift on going from 1,3-cyclohexadiene (τ 4.22) to benzene (τ 2.73) is -1.49 ppm. From Table I it may be seen that the ring current *t*-butyl proton shift on going from vinyl *t*-butylated systems to *t*-butylbenzene is about -0.3 ppm or 20% of the corresponding vinyl proton shift. We feel that this large shielding by about 1.5 ppm of the α and β protons is due mainly to an increase in the π-electronic charge densities at the α- and β-carbon atoms of cyclopentadienone relative to those of cyclopentenone. This interpretation is in agreement at the qualitative level with Hückel charge densities which are larger at both the α and β carbons of cyclopentadienone than at these positions of cyclopentenone. If we adopt the empirically estimated shift of 9.3 ppm per unit π-electron charge density,[31] we conclude that the α and β carbons of cyclopentadienone contain about 0.15 more π-electronic charge than do the respective carbons of cyclopentenone. Whereas

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(26) The absorption maxima of n $\rightarrow \pi^*$ transitions in cross-conjugated cycloalkadienones typically show a blue shift of about 20 mμ upon changing from hydrocarbon to alcohol solvents; see ref 19b.

(27) G. Berthier, *J. Chim. Phys.*, **50**, 344 (1953).

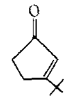
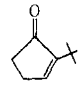
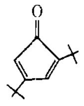
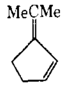
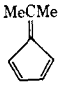
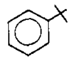
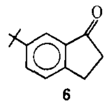
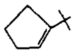
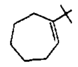
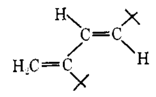
(28) A. Julg and A. Pullman, *ibid.*, **50**, 459 (1953). The authors considered interactions between only eight singly and doubly excited configurations. A more complete CI calculation would seem worthwhile.

(29) As cyclopentene and cyclopentadiene are alternate π systems, their π-electron densities will be unity except for secondary effects arising from the $(CH_2)_3$ and CH_2 parts, respectively. We presume that "ring currents" are negligible in both hydrocarbons; however, this may not be so for cyclopentadiene.

(30) Cyclopentadienone should exhibit an induced paramagnetic ring current [see J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966)] *if* **28** *(4n system) contributes enough to its ground state.*

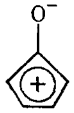
(31) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36** 2443 (1962).

Table I. Estimation of Vinyl Proton Chemical Shifts Expected for **18** and Dimethylfulvene[a]

	τ vinyl			
Compd	Found	Calcd	$\Delta\tau$	τ *t*-butyl (vinyl)
	4.40[b]			
	3.58			
 **1**	4.17			8.79
 **24**	2.78			8.83
 **18**	5.07 (α) 3.50 (β)	3.35 1.96	1.72 1.54	8.83, 8.82
	4.14 (α)[c] 3.71 (β)[c]			
	~3.66 (α)[d] ~3.66 (β)[d]	3.32 2.89	~0.34 ~0.77	
				8.68[e]
 **6**				8.65
 **23**				8.97
				9.00
				8.95, 8.97[f]

[a] Carbon tetrachloride solvent. Chemical shifts are in parts per million. [b] K. Wiberg, *J. Amer. Chem. Soc.*, **83**, 1226 (1961). [c] C. M. Sprecher, unpublished results. [d] The vinyl proton chemical shifts are nearly degenerate. The spin system is too tightly coupled to render an analyzable spectrum. [e] G. V. D. Tiers, private communication. [f] Intermediate in the synthesis of **20**. See Experimental Section.

this increased π charge must be regarded as a qualitative estimate, it seems certain that the π-electron density in cyclopentadienone is polarized more to within the ring than it is in cyclopentenone. Yet, apparently, **28** contributes more to the ground state of cyclopentadienone than does **29**, as the direction of the dipole moment of tetraphenylcyclopentadienone has been determined experimentally as being toward oxygen.[32]



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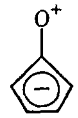

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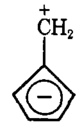

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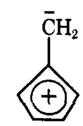

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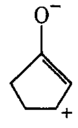
Fulvene is similar to cyclopentadienone with regard to its increased π-electron densities at the α and β positions relative to those (of unity) in 1,2-dihydrofulvene (see the appropriate data for 6,6-dimethylfulvene in Table I). Using charge densities resulting from the "ω" technique[33a] and the shift per unit charge taken above, calculated values for $\Delta\tau$, in Table I, for the α and β protons of 6,6-dimethylfulvene are 0.4 and 0.3 ppm, respectively. These are to be compared with those value tabulated. The dipole moment of fulvene, because of the absence of the counteracting inductive effect of oxygen, is in the opposite direction from that of cyclopentadienone. Consequently **30** contributes more to the ground state of fulvene than does **31**.[33b]

Ir Spectrum of 18. The only notable aspect of the ir spectrum of **18** is the fundamental stretching frequency of the carbonyl group. This is centered at 1708 cm^{-1}. As the conjugated carbonyl frequencies of **1**, **2**, **4**, **5**, **6**, **10**, **11**, **16**, **17**, **21**, **24**, **25**, and **27** are of comparable magnitudes (see Table VI), it appears that **28** is of no greater importance to the ground-state electronic structure of cyclopentadienone than **32** is to that of cyclopentenone.



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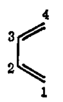
IV. Relative Reactivities of Diels-Alder Dimerizations

General Approach. In 1952, Brown successfully accounted for the relative reactivities of several Diels-Alder reactions involving aromatic "dienes" using the *para localization energy* method.[34] This method appears suited only for dimerizations having transition state structures approaching, π electronically, those of the products. However, Diels-Alder reactions of nonaromatic dienes generally are more reactive than those of aromatic ones and their transition state structures are expected to approximate the starting ones.[35] For these reactions, second-order perturbation methods[36] may best be used to account for reactivity differences. The perturbation method provides an estimate of the energy changes that result upon mixing the molecular orbitals of the reacting species in the transition state.

We consider that during the Diels-Alder dimerization, the primary interactions are between the diene and dienophile's π MO's at the bonding centers, *i.e.*, at C_1 and



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(32) A. DiGiacomo and C. P. Smyth, *J. Amer. Chem. Soc.*, **74**, 4411 (1952).

(33) (a) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949); (b) P. Yates, *Advan. Alicyclic Chem.*, **2**, 59 (1968).

(34) R. D. Brown, *Quart. Rev.* (London), **6**, 63 (1952). See also L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, p 297 ff.

(35) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(36) M. J. S. Dewar, "Advances in Chemical Physics," Vol. VIII, Interscience Publishers, New York, N. Y., 1965, p 65; K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology," P. Lowdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 513; L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

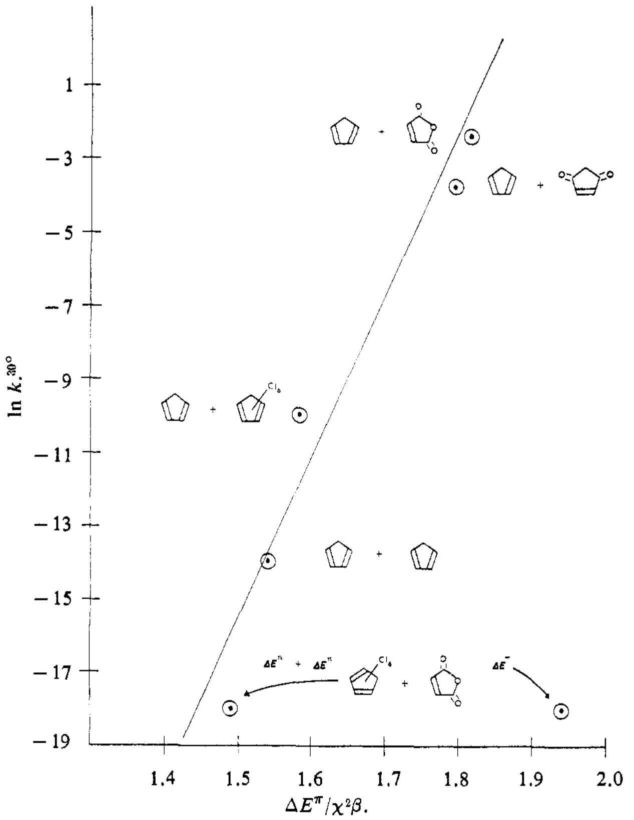


Figure 2. Correlation between ln $k^{30°}$ and $\Delta E^{\pi}/\chi^2\beta$ for five Diels–Alder reactions.

C_1 and at C_2 and C_4. Secondary interactions which may[37] or may not[23] be significant are neglected. The only interactions that lead to a net change in π-electronic energy in the transition state are those between occupied and unoccupied MO's. This energy change, ΔE^{π}, is given by[36]

$$\Delta E^{\pi} = 2\left(\sum_i^{\text{occ}}\sum_j^{\text{unocc}} - \sum_i^{\text{unocc}}\sum_j^{\text{occ}}\right)\frac{(c_{1i}c_{1j} + c_{4i}c_{2j})^2\chi^2\beta^2}{(E_i - E_j)_{\beta}} \tag{1}$$

where c_{ni} and c_{nj} are the coefficients of the nth atomic orbital of the ith and jth MO's of diene and dienophile, respectively, and $\chi\beta$ is the resonance integral between each of the two pairs of interacting atomic orbitals. As we assume the Diels–Alder reaction to be a concerted one, the two resonance integrals are considered equal.[38] In our calculations we have used Hückel wave functions and MO energies in units of β.

We would like a suitable correlation between observed rate constants for Diels–Alder dimerizations and calculated values of ΔE^{π} such that an estimation of the rate constant for the dimerization of cyclopentadienone can be made. If the differences in rates of a series of Diels–Alder reactions are governed primarily by differences in ΔE^{π}, then the logarithms of the second-order rate constants, k_r, for the members of the series are given as

$$\ln k_r = -\Delta E^{\pi}/RT + C \tag{2}$$

where C contains ln (kT/h) and logs of activation thermodynamic parameters that are constant for the series. Cancelling out a β from the top and bottom of eq 1 and dividing through by $\chi^2\beta$ leads to

$$\Delta E^{\pi}/\chi^2\beta = 2\left(\sum_i^{\text{occ}}\sum_j^{\text{unocc}} - \sum_i^{\text{unocc}}\sum_j^{\text{occ}}\right)(c_{1i}c_{1j} + c_{4i}c_{2j})^2/(E_i - E_j) \tag{3}$$

Taking

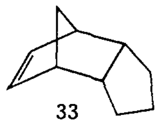
$$x = \Delta E^{\pi}/\chi^2\beta$$

eq 2 may be rewritten as

$$\ln k_r = -x(\chi^2\beta/RT) + C \tag{4}$$

According to eq 4, a plot of ln k_r *vs.* x for the series should be linear and have a slope equal to $\chi^2\beta/RT$.

An acceptable series of Diels–Alder reactions to provide a correlation curve from which k_r for cyclopentadienone dimerization could be extracted would be one in which all the members produce products having the basic skeleton of **33**. Such a series, then, must be restricted to five-membered ring diene and dienophiles containing substitutents of moderate size so as to minimize steric effects. Otherwise, the terms in C of eq 4 would vary with the member of the series. The correlation curve[39] for a series of Diels–Alder reactions which meets the above criteria is shown in Figure 2. Values of $k_r^{30°}$ were obtained from the literature.[40] Neglecting the point for the slowest reaction in Figure 2, the correlation curve gives $\chi^2\beta = -27$ kcal mole^{-1} and $C = -83$. The point corresponding to the reaction between maleic anhydride and perchlorocyclopentadiene is displaced from the correlation curve by a $\Delta E^{\pi}/\chi^2\beta$ equivalent to about 13 kcal mole^{-1}. The diene and dienophile of this reaction are unique among the series in that both bear groups having substantial bond dipole moments.[41] Consequently, the effect of electrostatic interactions in the reaction's transition state may be important.[24]



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The energy, ΔE^{μ}, arising from electrostatic interactions in the transition state of the reaction between maleic anhydride and perchloropentadiene was estimated from the approximate transition state structure **34**. The distance between the two molecules was taken as twice the van der Waals radius of carbon (3.2 Å).[42] To facilitate the calculation of ΔE^{μ}, we took the bond moment interactions between the C–O bonds of maleic anhydride and the C_5–Cl ones of the diene as approxi-

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(37) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965).

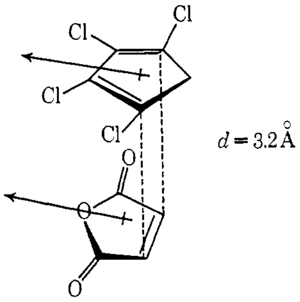
(38) The products of the Diels–Alder reactions that we consider contain no elements of symmetry. Consequently, equality of the two resonance integrals in the transition states and exact concertedness of the reactions are precluded.

(39) The HMO parameters used were: $\alpha_{\dot{O}} = \alpha + \beta'$, $\alpha_{\ddot{O}} = \alpha + 2\beta$, $\alpha_{Cl} = \alpha + 2\beta$, $\beta_{C=O} = 0.8\beta$, $\beta_{C-O} = \beta$, $\beta_{C-Cl} = 0.4\beta$. The methylene and dichloromethylene groups in cyclopentadiene (cyclopentenedione) and perchlorocyclopentadiene were treated as pseudoheteroatoms taking $\alpha_{CH_2} = \alpha + 1.5$, $\alpha_{CCl_2} = \alpha + 3\beta$, and $\beta_{C-CH_2} = \beta_{C-CCl_2} = 0.5\beta$ [see J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962)].

(40) A. Wasserman, "Diels–Alder Reactions," Elsevier Publishing Co., New York, N. Y., 1965, Chapter 5, and C. H. DePuy and E. F. Zaweski, *J. Amer. Chem. Soc.*, **81**, 4920 (1959).

(41) Molecular dipole moments for perchlorocyclopentadiene and maleic anhydride are 0.88 and 3.94 D, respectively. See D. H. Zyp and H. Gerding, *Rec. Trav. Chim. Pays-Bas*, **77**, 682 (1958); and S. Soundararajan and M. J. Vold, *Trans. Faraday Soc.*, **54**, 1155 (1958).

(42) W. C. Herndon and L. H. Hall, *Theor. Chim. Acta*, **7**, 4 (1967).



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mating zero.[43] The electrostatic interaction energy difference between ground and transition states, ΔE^{μ}, was estimated, using cgs units, from the point dipole expression[44]

$$\Delta E^{\mu} = \sum_i \sum_j [\vec{\mu}_i \cdot \vec{\mu}_j - 3(\vec{\mu}_i \cdot \vec{R}_{ij})(\vec{\mu}_i \cdot \vec{R}_{ij})/\vec{R}_{ij}^{\,2}]/\epsilon \vec{R}_{ij}^{\,3} \quad (5)$$

where $\vec{\mu}_i$ and $\vec{\mu}_j$ are the interacting dipole vectors on the diene and dienophile, $\vec{R}_{ij}$ are the vectors connecting the dipole centers, and ϵ is the dielectric constant between the interacting dipoles. Using $\mu_{H \rightarrow C} = +0.4$ D, bond moments given by Smith,[45] recommended positions of dipole centers,[46] and $\epsilon = 2$ (hydrocarbon), ΔE^{μ} was estimated to be 12 kcal mole^{-1}. Adding ΔE^{μ} to ΔE^{π} moves the correlation point for the reaction between maleic anhydride and perchlorocyclopentadiene close to the curve, as seen in Figure 2. Although the estimate of ΔE^{μ} cannot be considered quantitative, we feel that it shows that electrostatic repulsion in the transition state is the major reason for the bad correlation between ln $k^{30°}$ and $\Delta E^{\pi}/\chi\beta$ for the maleic anhydride–perchloropentadiene reaction.

Estimated Rates of Dimerizations Involving Cyclopentadienone. If cyclopentadienone has a molecular dipole moment comparable to that for the tetraphenyl derivative, *i.e.*, 3.43 D,[32] electrostatic interactions are expected to affect its dimerization rate as well as those of reactions between it and other dipolar dienes and dienophiles. So as to estimate these rates at 30°, eq 2 may be rewritten as

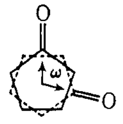
$$\ln k_r^{30°} = -1.66(\Delta E^{\pi} + \Delta E^{\mu}) - 83 \quad (6)$$

Values of ΔE^{π} were obtained from eq 1 where $\chi^2\beta = -27$ kcal/mole, as determined from the slope of the correlation line in Figure 2. The constant -83 in eq 6 is the value of C in eq 2 as determined from the intercept of the correlation line in Figure 2. Values for ΔE^{μ} to be used in eq 6 were estimated according to the following discussion.

If the basic transition state structure **34** is adopted and if it is assumed that the centers of the molecular dipole vectors are located at the centers of the five-membered rings and are connected by orthogonal vectors, $\vec{R}$, eq 5 simplifies to

$$\Delta E^{\mu} = \vec{\mu}_A \cdot \vec{\mu}_B / \epsilon \vec{R}^3 \quad (7)$$

where $\vec{\mu}_A$ and $\vec{\mu}_B$ are the molecular dipole moments of molecules A and B, and $\vec{R}$ is the distance between dipoles in the transition state. Taking $\vec{R} = 3.2$ Å and $\epsilon = 2$, ΔE^{μ} is given by



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$$\Delta E^{\mu} = 0.919\mu_A\mu_B \cos \omega \text{ kcal mole}^{-1} \text{ D}^{-2} \quad (8)$$

where ω is the angle included by $\vec{\mu}_A$ and $\vec{\mu}_B$. Taking 3.43 D as the dipole moment of cyclopentadienone and $\omega = 108°$ as shown in **35**, ΔE^{μ} is -3.3 kcal/mole.

Estimated second-order rate constants for several Diels–Alder dimerizations involving cyclopentadienone are collected in Table II. That for the dimerization of cyclopentadienone is about 10^8 M^{-1} sec^{-1}. The small energy gap between the highest occupied and lowest unoccupied MO's of cyclopentadienone (see Figure 1) is largely responsible for the large magnitude of this estimated rate constant, since perturbations arising from mixing of the highest occupied and lowest unoccupied states of the Diels–Alder reactants normally will dominate the terms in eq 1. As secondary[37,42] interactions, *i.e.*, those between the diene and dienophile's π MO's and nonbonded AO's (*e.g.*, carbonyl oxygen), will combine to increase the π stabilization (ΔE^{π}) in the transition state, the rate of cyclopentadienone may approach that for diffusion control ($k_D \approx 10^{10}$ M^{-1} sec^{-1}).

Cyclopentadienone is expected, according to the data in Table II, to react with cyclopentadiene exclusively as a dienophile. This expectation is born out experimentally.[2] We predict from Table II that maleic anhydride should intercept cyclopentadienone more effectively than cyclopentadiene. The reverse, however, has been observed.[2] Although eq 7 surely will render a high limit estimation of the dipolar attraction (ΔE^{μ}) for the maleic anhydride–cyclopentadienone dimerization,[47] it is surprising that maleic anhydride has not been found to trap cyclopentadienone efficiently.

Table II. Estimated Rate Constants for Diels–Alder Reactions of Cyclopentadienone[a]

Dienophile	Diene	ΔE^{π}, kcal/mole	ΔE^{μ}, kcal/mole	ω	Log $k^{30°}$, M^{-1} sec^{-1}
CPDO	CPDO	−57.5	−3.3	108°	8
CPDO	CP	−54.5	0.0		3
CP	CPDO	−44.6	0.0		−4
MA	CPDO	−48.5	−12.4	180°	8

[a] CPDO = cyclopentadienone, CP = cyclopentadiene, and MA = maleic anhydride.

Estimated Rates of Dimerizations of Cyclopentadienone Derivatives. Estimated half-lives ($t_{1/2}^{30°}$) for Diels–Alder dimerizations of 1 M solutions of several

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[43] This is reasonable as (1) the distances between interacting dipoles are large relative to those for the other interactions and (2) the scalar products of the C=O and C—Cl bond moment vectors are small.

[44] J. H. Jeans, "Mathematical Theory of Electricity and Magnetism," 5th ed, Cambridge University Press, London, 1963, p 377.

[45] J. W. Smith "Electric Dipole Moments," Butterworth and Co., Ltd., London, 1955, p 92.

[46] L. Meyer, *Z. Phys. Chem.*, **38**, 27 (1930); F. T. Wall, *J. Amer. Chem. Soc.*, **62**, 800 (1940); C. P. Smyth, R. W. Dornte, and E. B. Wilson, Jr., *ibid.*, **53**, 4242 (1931). These references recommend various positions for the dipole centers. The calculated ΔE^{μ} varied between 11.7 and 12.5 kcal/mole, depending upon the dipole centers adopted.

[47] The model used for the derivation of eq 6 will lead to an upper limit of ΔE^{μ}, as the negative term in eq 5 is neglected and $|R|$ is underestimated. Also, it is unlikely that the molecular planes of the diene and dienophile are parallel in the transition state, as assumed (see **34**).[23] Any deviation from this parallel configuration will lead to a reduction in $|\Delta E^{\mu}|$.

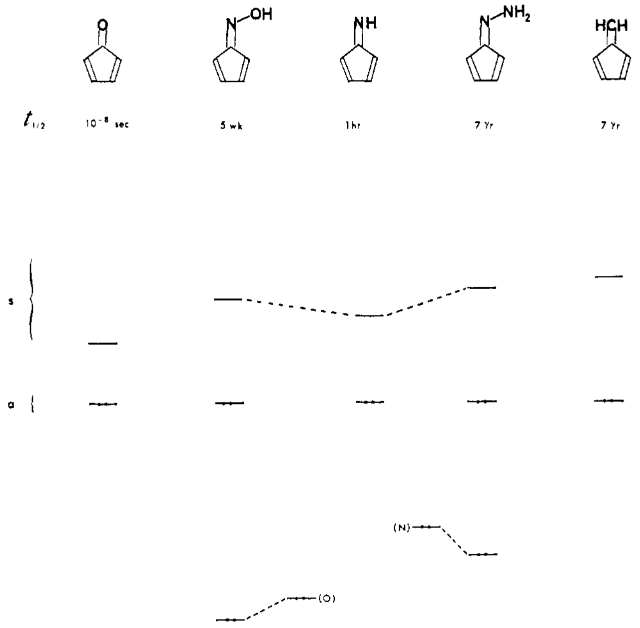
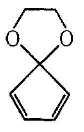


Figure 3. Correlation between estimated values of $t_{1/2}^{30°}$ (1 *M*) for several cyclopentadienone derivatives and energy gaps between their highest occupied and lowest unoccupied molecular orbitals.

derivatives of cyclopentadienone are given in Figure 3 together with energy diagrams showing the relative energies of the corresponding highest occupied and lowest unoccupied MO's. Values of $t_{1/2}$ (1 *M*) were estimated from eq 6 where ΔE^{μ} was neglected except for cyclopentadienone. The relative $t_{1/2}$ values are seen from Figure 3 to parallel the energy gaps between the highest occupied and lowest unoccupied MO's of the systems undergoing dimerization. As the highest occupied MO's of the systems shown in Figure 3 are antisymmetric with respect to their vertical molecular planes (or pseudoplanes) of symmetry, they are unaffected by the natures of atoms laying along these planes. Consequently, the energy gaps between the highest occupied and lowest unoccupied MO's will be governed by changes in the energies of the latter which are symmetric with respect to the vertical molecular planes.

5-Iminocyclopentadiene, which has not yet been synthesized, is expected to be less reactive than cyclopentadienone and more reactive than fulvene, primarily because the electronegativity of nitrogen falls between those of oxygen and carbon. π bonding a nitrogen or oxygen atom to the nitrogen of 5-iminocyclopentadiene should increase the energy of the lowest unoccupied MO and not effect that of the highest occupied one (whose coefficient at nitrogen is zero). As oxygen is more electronegative than nitrogen, conversion of 5-iminocyclopentadiene to oximinocyclopentadienone will lead to less of an increase in the energy of the highest unoccupied MO than will conversion to the hydrazone derivative of cyclopentadienone. The hydrazone derivative of cyclopentadienone has been found to be a stable low melting material which can be distilled unaltered.[48] Oximinocyclopentadienone, however, has not been isolated yet as a monomer.[49]

Dimerizations of Cyclopentadienone Ketals. Cyclopentadienone is not unique in its pronounced reactivity toward Diels-Alder dimerization. Eaton and Hudson found that its ethylene ketal (**36**) dimerizes 500,000 times faster than does cyclopentadiene.[50] As the five-membered ring π system of **36** would not seem to differ greatly from that of cyclopentadiene, the origin of this special reactivity is intriguing. As for cyclopentadienone (see **35**), dipolar interactions in the transition state for dimerization are expected to be attractive. However, detailed calculation of ΔE^{μ} from bond moments and eq 5 gave $\Delta E = -0.3$ kcal/mole. Consequently, electrostatic interactions are not expected to influence significantly the dimerization rate of **36**.



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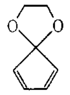
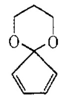
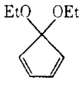
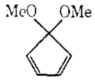
The data collected in Table III show a parallel trend between $\lambda_{\max}$ for the lowest energy $\pi \rightarrow \pi^*$ transitions for a number of cyclopentadienone ketals, including cyclopentadiene, and the rates of their dimerizations. Apparently, introduction of the ketal function on C_5 of cyclopentadiene leads to a reduction of the energy gap between the highest occupied and lowest unoccupied MO (*i.e.*, bathachromic shift of lowest energy $\pi \rightarrow \pi^*$ transition) and thence to an increased reactivity toward Diels-Alder dimerization. This effect is predicted, if the nonbonded AO's on the oxygen atoms of the ketals interact with the cyclopentadiene MO's at carbons 1 and 4.[1] Simmons and Fukunaga have developed a general theory for such interactions, which they call *spiroconjugation*, and have demonstrated its utility in qualitatively understanding many ultraviolet spectral trends.[51]

Table III. Ultraviolet Spectra and Relative Rates of Dimerization of Some Cyclopentadienone Ketals

Diene	$\lambda_{\max}$, mμ	Log ε	k/k_{ref}[a]
	241[a]	3.5[b]	1.0
	280[b] 280[c] 196[c]	 3.04[c] 3.35[c]	5 × 10⁵
	272[a]		6500
	270[a]		465
	270[a] 270[d] 195[d]	 3.09[d] 3.34[d]	790

[a] Reference 50. [b] S. L. Friess and V. Boekelheide, *J. Amer. Chem. Soc.*, **71**, 4145 (1949). [c] Compound **12**, this work. [d] Compound **8**, this work.

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(48) K. Hafner, G. Schulz, and K. Wagner, *Ann. Chem.*, **678**, 39 (1964).

(49) J. Thiele, *Ber.*, **33**, 669 (1900); W. Doering and C. H. DePuy, *J. Amer. Chem. Soc.*, **75**, 5955 (1953).

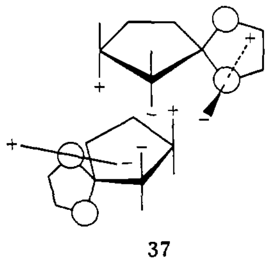
(50) P. E. Eaton and R. A. Hudson, *ibid.*, **87**, 2769 (1965).

(51) H. E. Simmons and T. Fukunaga, *ibid.*, **89**, 5208 (1967).

If for simplicity we consider the nonbonded electrons on the oxygens of **36** as occupying 2p and sp^2 orbitals, we note that the 2p AO's may interact with the 2p AO's on carbons 1 and 4 of cyclopentadiene. Also, the 2p AO's on the oxygens of **36** form two combinations under C_{2v} symmetry; one belonging to the a_2 and the other to the b_2 symmetry species (see Figure 4 in which the oxygen MO's are probably closer to being degenerate than shown). As only states of the same symmetry species will mix, the highest occupied MO of cyclopentadiene will increase in energy and the lowest unoccupied MO will remain unaltered upon mixing the oxygen and cyclopentadiene π systems (see Figure 4). Consequently, **36** will have a smaller energy gap between the highest occupied and lowest unoccupied MO's than will cyclopentadiene. However, the degree of mixing which is determined in part by the resonance integral for the oxygen–carbon interaction is not likely to be strong enough to account solely for the enormous difference between the rates of dimerization of **36** and cyclopentadiene.[52]

Another interaction that will contribute to the high reactivity of **36** is expected to occur in the transition state for its dimerization. If **37** is taken as approximating the transition state structure, interactions between a filled oxygen p orbital of one molecule and both unoccupied cyclopentadiene MO's at carbons 2 and 3 of the second molecule, and *vice versa*, will be bonding or stabilizing. The magnitude of the stabilization energy, $\Delta E^{\pi,p}$, will be directly proportional to the square of the resonance integral for the interaction.

The combined ground and transition state effects that have been discussed above may account for the special reactivity of **36**. Both effects correctly predict a decrease in rate of dimerization upon going from **36** to the propylene, dimethyl, or diethyl ketals of cyclopentadienone. In these latter ketals, the stereorelationships between the oxygen and cyclopentadiene p orbitals surely will be less than optimal for maximum interactions. This is because nonbonded alkyl group repulsions in the dialkyl ketals and torsional and angle strains in the dioxane ring of the propylene ketal will inhibit conformations approaching the optimum one of the dioxolan ring in **36**.



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Experimental Section

Ultraviolet, ir, and nmr spectral data and microanalytical data on isolable compounds **1**–**27** are collected in Tables IV–VI.

3-*t*-Butylcyclopentadienone Ethylene Ketal (8) and Its Dimer (9). A solution of 349 g of 3-*t*-butylcyclopentanone,[53] 0.2 g of *p*-toluenesulfonic acid, and 150 ml of ethylene glycol in 750 ml of benzene was refluxed under a water separator for 24 hr. Addition of sodium methoxide, followed by distillation of the benzene, gave an oily residue which was distilled to give 387 g (85%) of 3-*t*-butylcyclopentanone ethylene ketal: bp 54° (1.0 mm); n^{25} 1.4535.

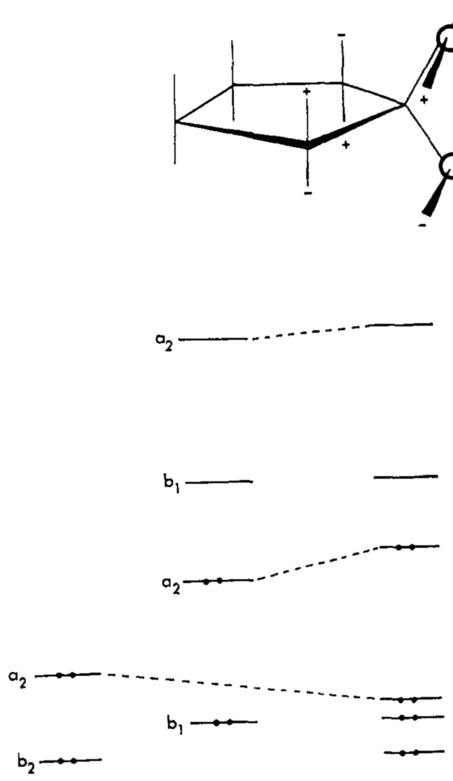

Figure 4. Energy level diagrams of (1) isolated cyclopentadiene and oxygen π systems (left) and (2) after mixing (right).

Bromine (143 g, 0.895 mole) was added to a solution of 81.3 g (0.430 mole) of the ketal in 200 ml of anhydrous ether at a rate such that the color of the bromine was always present. On completion of the addition, the solution was swept with dry nitrogen, in order to remove most of the hydrobromic acid. Ether was replaced as necessary. The cold solution was poured into a saturated sodium carbonate solution and the ethereal layer was separated and dried.

Table IV. Microanalytical Data

Compd	Empirical formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
1	$C_9H_{14}O$	78.21	10.21	77.98	9.88
2	$C_9H_{13}OBr$	49.76	5.99	49.52	6.00
4	$C_{18}H_{24}O_2$	79.37	8.88	79.43	8.98
5	$C_{14}H_{18}O$	83.12	8.97	82.84	8.70
6	$C_{17}H_{24}O$	83.55	9.90	83.92	9.75
7	$C_{20}H_{28}O_3$	75.91	8.92	75.67	9.11
8	$C_{11}H_{16}O_2$	73.30	8.95	73.07	9.10
9	$C_{22}H_{32}O_4$	73.30	8.95	73.15	8.78
10	$C_{10}H_{28}O_3$	75.91	8.92	75.44	8.42
11	$C_{18}H_{24}O_2$	79.37	8.88	78.27	8.43
12	$C_{11}H_{18}O_2$	72.49	9.96	73.03	10.53
13, **14**	$C_{16}H_{24}O_2$	77.37	9.74	77.54	9.45
15	$C_{15}H_{28}O_2$	74.95	11.74	75.24	12.03
16	$C_{13}H_{21}OBr$	57.14	7.69	57.11	7.69
17	$C_{13}H_{21}OBr$	57.14	7.69	57.11	7.73
18	$C_{14}H_{26}O_4$	65.08	10.14[a]	65.36	10.31[a]
20	$C_{16}H_{20}O_3$	73.82	7.74	73.51	7.89
21	$C_{26}H_{40}O_2$	81.20	10.48	80.92	10.19
22	$C_{11}H_{23}N$	78.03	13.69	78.31	13.50
23	C_9H_{16}	87.02	12.98	87.37	12.56
24	$C_9H_{14}O$	78.21	10.21	78.06	9.99
25	$C_9H_{13}OBr$	49.78	6.03[b]	49.71	5.87[c]
27	$C_{18}H_{24}O_2$	79.37	8.88	79.21	8.72

[a] Neutralization equivalent calculated and found to be 129. [b] % Br = 36.81. [c] % Br = 36.83.

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(52) The Mulliken overlap integral for the carbon–oxygen interaction is <0.009.

(53) H. Pines and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **61**, 2728 (1939).

Table V. Nmr Spectral Data[a]

Compd	$\tau_{t\text{-Bu}}$	m[b]	τ_H	n[c]	J_{ij}	i,j[d]
1	8.79	3	4.17	2	$\lvert 1.8\rvert$	2,4
			7.23–7.90	4–5		
2[e]	8.65	3	3.38	2	$\lvert 0.4\rvert$	2,4
			4.84	4	1.2	4,5a
			7.24	5a	6.4	4,5b
			6.97	5b	−19.2	5a,5b
4	9.00	9	7.20	2	$\lvert 1.0\rvert$	4,6
	8.78	5	4.00	4	$\lvert 1.7\rvert$	1,8
			4.24	8	$\lvert 3.9\rvert$	7,8
			6.38–6.92	1,7,6	$\lvert 9\rvert$	1,2 + 2,6
5	8.82	5	6.82–7.02	1,7	$\lvert 5.0\rvert$	1,2
			7.28	2	$\lvert 5.9\rvert$	2,6
			4.37	4	$\lvert 1.1\rvert$	4,6
			6.62	6	$\lvert 4.3\rvert$	6,7
			3.98–4.38	8,9		
			8.14–8.54	10		
6	9.05	3	7.48	2	$\lvert 5\rvert$	2,3
	8.65	6	6.85	3	$\lvert 8.0\rvert$[f]	4,5
			2.47–2.55	4,5		
			2.35	7		
7	9.05	9	7.01–7.37	1,2,7	$\lvert 5\rvert$	6,7;6,2
	8.82	5	4.23	4		
			6.52	6		
			4.65	8		
			6.10–6.24	3′,4′[g]		
8[h]	8.92	3	4.619	2	1.67	2,4
			3.899	4	2.03	2,5
			4.133	5	5.80	4,5
			6.16	3′,4′[g]		
9	8.87	5	7.57	1	$\lvert 5.0\rvert$	1,2
	9.02	8	7.29	2	$\lvert 1.5\rvert$	1,7
			4.80	4	$\lvert 3.8\rvert$	1,9
			6.61	6	$\lvert 7.6\rvert$	2,6
			7.36	7	$\lvert 0.4\rvert$	2,9
			4.21	9	$\lvert 0.2\rvert$	4,6
			6.15–6.35	3′,4′,3″,4″[g]	$\lvert 3.9\rvert$	6,7
					$\lvert 1.6\rvert$	7,9
10	8.77	5	7.10–7.36	1,2,7		
	9.03	8	4.23	4		
			6.43	6		
			4.30	9		
			6.08–6.28	3′,4′[g]		
11	8.72	5	7.12	2		
	8.98	8	4.05	4		
			6.52–6.92	1,6,7		
			3.90	9		
12	8.88	3	4.32	2		
			3.85	4,5		
			6.73	OCH_3		
13	8.92	4	6.85	OCH_3		
			6.92	OCH_3		
14	9.05	8	6.87	OCH_3		
			6.97	OCH_3		
15	9.15	2,4	6.1–6.3	3′,4′[g]		
	9.05					
16	8.85	2,4	2.77	3	0.0	3,5
	8.80		7.07	5		
17[i]	8.80	3,5	4.15	2		
	8.89		6.87–6.91	4		
17[j]					1.7	2,4a
					2.1	2,4b
					$\lvert 20\rvert$	4a,4b
18	8.82	2,4	3.50	3	$\lvert 1.7\rvert$	3,5
	8.83		5.07	5		
19	8.97	3	4.27	4		
	8.87	5				
20	8.57	3,5	2.17	4,6	$\lvert 1.7\rvert$	4,6
	8.48		2.20			
21	9.02	1,6	7.12	2	$\lvert 1.8\rvert$	7,9
	8.95		3.35	5		
	8.88	4,8	6.88	7		
	8.83		4.13	9		
22[k]	9.17	3	7.90	NCH_3		
	9.18		7.91			
23	8.97	1	4.73	2		
24	8.83	2	7.33–7.83	4,5	$\lvert 2.6\rvert$	3,4
			2.78	3		
25[e]	8.20	2	3.13	3	$\lvert 2.6\rvert$	3,4
			5.00	4	1.6	4,5a
			7.33	5a	6.5	4,5b
			7.01	5b	$\lvert 19.6\rvert$	5a,5b
27	8.85	4	6.77	1	4.9	1,2
	8.90	7	7.18	2	6.3	2,6
			3.13	5	2.6	5,6
			6.70	6		
			3.82	8,9		

[a] 20% wt/wt in CCl_4 unless otherwise noted. [b] Number of the atom bearing the *t*-butyl group. [c] Numbers of the carbon bearing hydrogen. [d] Numbers of the two carbons bearing coupled hydrogens. [e] The spectrum was analyzed as arising from an ABMX system. Geminal couplings were assumed to be negative. [f] Obtained from nmdr experiment, see part I of text. [g] Ethylene ketal resonances. [h] The spectral parameters resulted from a detailed spectral analysis which will be reported elsewhere. [i] An insufficient number of transitions were observed to effect a spectral analysis. [j] ABX analysis results for **17** in acetone. [k] Mixture of stereoisomers.

Distillation of the ether at reduced pressure was followed by recrystallization of the residue from methanol to give 89 g (61%) of 2,4-dibromo-3-*t*-butylcyclopentanone ethylene ketal, mp 101–102°.

Anal. Calcd for $C_{11}H_{18}O_2Br$: C, 38.62; H, 5.60; Br, 46.72. Found: C, 38.76; H, 5.31; Br, 46.78.

A slurry of 34.0 g (0.10 mole) of the dibromo ketal and 21 g (0.39 mole) of sodium methoxide in 75 ml of dimethyl sulfoxide was stirred at 25° for about 40 hr. When only **8** and **9** could be found by nmr in an aliquot, 200 g of ice was added to the slurry. Filtration of the resulting paste gave a wet solid which was taken up in pentane, washed with water, and dried. Distillation of the pentane at reduced pressure gave a solid residue which was sublimed at 45° (0.5 mm) to give 9.0 g (50%) of **8**, mp 63–65°. The sublimation residue was 7.2 g (40%) of **9**. An analytical sample of **9**, prepared by recrystallization from pentane, melted at 107–110°.

If any bromine-containing intermediate products remained when the dehydrohalogenation reaction was worked up, they interfered seriously in the purification of **8**.

5,8-Di-*t*-butylspiro[*endo*-bicyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one-10,2′-[1′,3′]dioxolane] (10). A solution of 1.0 g of **9** and 0.10 g of *p*-toluenesulfonic acid in 10 ml of acetone was allowed to stand for 15 min. Then, 1.0 ml of saturated sodium bicarbonate solution was added and the acetone was distilled. The residue was taken up in ether, and the ether solution was washed with water and dried. The ether was distilled to give 0.90 g (100%) of **10**, mp 118–119°. An analytical sample, prepared by recrystallization from pentane, melted at 119–121°.

***endo*-5,8-Di-*t*-butyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione (11).** A suspension of 1.15 g (0.00364 mole) of **10** in 50 ml of aqueous sulfuric acid was refluxed for 22 hr. The aqueous mixture was extracted with ether and the ethereal extract was dried. Evaporation of the ether left a gummy residue which was recrystallized from 50 ml of pentane to give 0.25 g (25%) of solid, mp 114–118°. The mother liquor was concentrated and cooled to give 0.15 g of solid, mp 95–105°. The first crop was recrystallized from pentane to give an analytical sample, mp 124–126°.

3-*t*-Butylcyclopentadienone Dimethyl Ketal (12). A solution of 5.0 g of **8** in 25.0 ml of anhydrous methanol was mixed rapidly with 100.0 ml of 0.00184 *M* methanolic sulfuric acid. The solution was stirred for 900 sec at 25° and then 10 ml of 0.1 *M* methanolic sodium methoxide was added. The methanolic solution was concentrated to 25 ml and 30 ml of pentane was added. The resulting mixture was washed with water and the pentane phase dried. Distillation of the pentane followed by distillation of the residue under reduced pressure gave 3.5 g (70%) of **12**, bp 35–45° (1 mm), which was 90% pure by the methyl resonances in its spectrum. Redistillation afforded a center cut of 1.5 g (99% pure), bp 57° (1.8 mm).

Table VI. Ir[a] and Uv[b] Spectral Data

	Infrared		Ultraviolet			
Compd	$\nu_{C=O}$	$\nu_{C=C}$	λ_{max} (isooctane)	Log ϵ	λ_{max} (methanol)	Log ϵ
1	1708	1600				
2	1718	1590				
3			200	4.71	210	
			380	>1.9		
4	1710	1600	197	4.14	202	3.94
	1790		223	4.00	231	4.04
			316	1.67	312	1.89
			329	1.77		
			343	1.71		
5	1698	1590	193	3.88	201	3.73
			225	4.02	233	4.07
			318	1.56	309	1.81
			331	1.64		
			345	1.56		
6	1705					
7	1695	1595				
8			196	3.35	203	3.14
			280	3.04	280	3.01
10	1695	1590				
11	1700	1590				
12			195	3.34	203	3.11
			270	3.09	271	3.01
16	1700	1603				
17	1709	1610				
18	1708	1610	210	3.86	217[c]	3.87
		1630	390	2.43	395[c]	2.36
20	1770					
21	1700		193	4.12	203	3.88
	1765		226	3.80	231	3.80
			324	1.79	334	1.96
			337	1.91		
			351	1.86		
23		1630				
24	1700	1620				
25	1710	1610	219	4.32	222	4.03
			334	1.55	323	1.59
27	1775		226	3.82		
	1700		322	1.79		
			336	1.88		
			351	1.82		

[a] Wave numbers are given in cm^{-1}. [b] Wavelengths are given in mμ. [c] In ethanol.

3-*t*-Butyl-5,5-dimethoxytricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (13) and 8-*t*-Butyl-10,10-dimethoxytricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (14). A mixture of 1.0 g of **12** and 1.0 g of cyclopentadiene was heated in a sealed tube at 100° for 4 hr. Distillation of the mixture gave 1.1 g of a mixture of **13** and **14**, bp 70–90° (0.2 mm).

Analysis of the mixture by nmr showed it to contain 68% **13** and 28% **14**. The remaining 4% of the methyl area arose from unidentified products. A portion of the mixture in carbon tetrachloride was hydrolyzed in an nmr tube with 20 μl of water and 1 drop of trifluoroacetic acid. The larger of the *t*-butyl resonances shifted by 5 cps while the smaller of the two did not shift. The methoxyl resonance corresponding to the major isomer disappeared while that for the minor isomer remained unchanged.

***endo*-5-*t*-Butyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (5).** A solution of 800 mg of the mixture of **13** and **14** obtained from the previous reaction, and 100 mg of *p*-toluenesulfonic acid in 10 ml of acetone was distilled at atmospheric pressure and the residue was taken up in pentane. The pentane solution was washed with water, dried with magnesium sulfate, and then the pentane was distilled. On standing, the oily residue solidified. It was recrystallized from pentane to give 51 mg (7.7%) of **5**, mp 51–52°.

3-*t*-Butyl-2-cyclopentenone (1). A solution of 200 g (2.0 moles) of pinacolone in 200 ml of ether was cooled to 5° and 10 ml of concentrated sulfuric acid was added. The mixture was recooled to 5° and 320 g (2.0 moles) of bromine was added at a rate such that the temperature remained less than 10°. When the addition was complete, the mixture was poured onto ice. The ether layer was separated, washed with water and 10% sodium bicarbonate solution, and dried over magnesium sulfate. The ether was evaporated at reduced pressure to give 344 g (96%) of crude 1-bromo-3,3-dimethylbutan-2-one which was suitable for the following preparation. Distillation gave a 75% yield of pure material, bp 73–77° (12 mm) [lit.[2] bp 77–78° (15 mm)].

6,6-Dimethylheptane-2,5-dione was prepared from crude 1-bromo-3,3-dimethylbutan-2-one in 58% yield by a reported procedure.[54] Over a period of 13 hr, 50 g (0.321 mole) of this material was added dropwise to a refluxing suspension of 19 g (0.487 mole) of sodium amide in 1 l. of benzene. The mixture was stirred vigorously during the addition and for 0.5 hr thereafter. Then, 10 ml of water was added dropwise, followed by the addition of 100 ml of 30% sulfuric acid. The benzene layer was separated, washed with water, and dried over magnesium sulfate. The benzene was removed by distillation and the residue was distilled at reduced pressure to give 12.9 g (29.2%) of **1**, bp 100° (8.0 mm). The 2,4-dinitrophenylhydrazone of **1** melted at 197–200°.

3-*t*-Butyl-4-bromo-2-cyclopentenone (2). A mixture of 5.0 g (0,0362 mole) of **1**, 7.1 g (0.0400 mole) of N-bromosuccinimide, 100 mg of benzoyl peroxide, and 50 ml of carbon tetrachloride was refluxed for 1 hr at which time all solid material floated to the surface of the mixture. The solid material was removed by filtration and washed with carbon tetrachloride. The combined filtrates were washed with water and dried overmagnesium sulfate. The carbon tetrachloride was evaporated under reduced pressure and the residue was crystallized from pentane. Two recrystallizations from pentane gave 4.2 g (53%) of **2**, mp 39–40°.

***endo*-5,9-Di-*t*-butyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione (4).** A. A mixture of 1.0 g (0.00460 mole) of **2** and 5.0 ml of triethylamine was left for 0.5 hr. Then, 20 ml of water was added and the mixture was extracted with two 10-ml portions of pentane. The combined extracts were washed with sodium hydrogen sulfate until the wash was acid to litmus, and then dried over magnesium sulfate. Evaporization of the pentane left a solid residue that was recrystallized twice from pentane to give 0.40 g (64%) of **4**, mp 63–65°. The pentane was distilled from the other liquors and an nmr spectrum of the residue was determined. It was identical in all respects with that of the crystalline material, except for two absorptions at τ 8.67 (**2**) and 8.73 (**11**) which comprised 10% of the total methyl area.

B. A solution of 220 mg of **8**, 0.1 ml of water, and 100 mg of *p*-toluenesulfonic acid in 5 ml of methanol was allowed to stand for 5 min. The initially yellow solution decolorized rapidly. Water (20 ml) was added and the mixture was extracted with 15 ml of pentane in three portions. The pentane extract was dried and the pentane was distilled. The residue was crystallized from 2 ml of pentane to give 66 mg of crude **4**, mp 60–70°. One recrystallization from 1 ml of pentane gave 33 mg of pure **4**, mp 70–72° The mixture melting point with the material prepared from **2** was not depressed and the nmr spectra of the two materials were identical.

3-*t*-Butylcyclopentadienone (3). Dry nitrogen was passed through molten **2** which was maintained at 70° and 1 mm pressure and then through a bed of anhydrous potassium carbonate (20–40 mesh) which was heated to 200°. Figure 5 shows the apparatus used. The optimum nitrogen flow rate was *ca.* 7 ml/min at standard temperature and pressure. The bromide (**2**) was carried to the column at a rate of *ca.* 20 mg/hr. The effluent gases from the column contained **3** which was collected in one of the following ways.

(a) The effluent from the column was directed onto a glass surface *ca.* 2 mm from the capillary end. The surface was cooled to −196° with liquid nitrogen. The yellow material which accumulated over a period of 1 hr was mixed with 1 ml of cyclopentadiene and warmed to room temperature. The excess cyclopentadiene was then removed under reduced pressure. The residue was taken up in carbon tetrachloride and analyzed by nmr. In a typical run the ratio of **4**:**5** was 1:1. The identity of the products was confirmed by adding known samples of **4** and **5** to the reaction product and observing that no new methyl resonances could be observed in the nmr spectrum.

(b) The effluent from the capillary was directed into 50 ml of cyclopentadiene which was stirred and cooled to −80°. After 2.5 hr the excess cyclopentadiene was removed under reduced pressure. The residue was analyzed by nmr and found to consist of 92% **5** and 8% **4**.

(c) The effluent from the capillary was directed for 5 min onto 50 ml of stirred isooctane or methanol cooled to −80°. The resulting solution was placed in a 1-cm uv cell which was precooled to

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(54) N. Mesina and E. V. Brown, *J. Amer. Chem. Soc.*, **74**, 920 (1952).

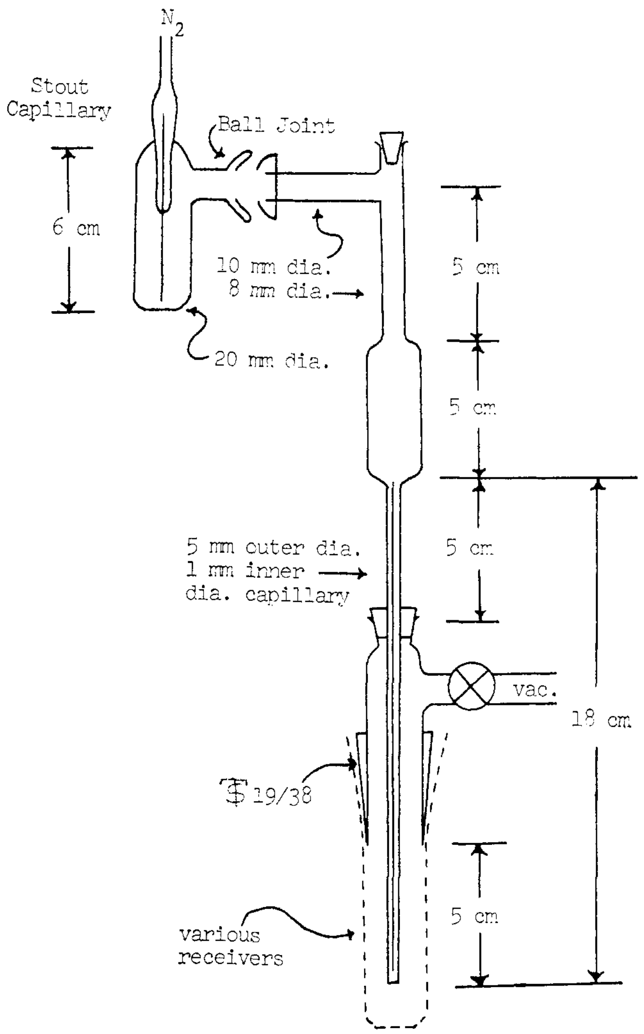

Figure 5. Schematic of cyclopentadienone generator.

−60° and the ultraviolet spectrum was recorded in the region of 200 mμ. The optical density of the isooctane solution at 200 mμ did not change over a period of 15 min. The sample was warmed to 25°, cooled again, and the spectrum recorded. It was identical with that of **4**.

(d) A solution of **3** in isooctane was collected in the usual way. A 5.0-ml aliquot was diluted with 27 ml of isooctane at −80° and the optical density was recorded at 200 mμ and −60°. The remainder of the original solution was warmed to 25° for 15 min. An aliquot of this solution gave the spectrum of **4** and the optical density at 223 mμ was recorded. The value for the extinction coefficient for **3** at 200 mμ was calculated from the dilution factor, the extinction coefficient for **4**, Beers law, and the assumption that the initial solution contained 92% **3**.

(e) A sample collected as in a was transferred, with isooctane or methanol, to a cell which had been precooled to −60°. The spectrum was scanned repeatedly from 500 to 320 mμ. The λ_{max} was estimated to be the wavelength at which the optical density was decreasing most rapidly. An estimate of the minimum extinction coefficient in isooctane was made from the initially recorded optical density and the optical density due to the dimer after reaction completion.

3,6-Di-*t*-butyl-1-indanone (6). A 2.0-g portion of **4** was heated to 160° for 45 min and then to 180° for 20 min. The product was cooled to room temperature and mixed thoroughly with 2.0 ml of phosphoric acid for 5 min. The viscous material was taken up in ether. The ether solution was washed with water and aqueous sodium bicarbonate and finally dried. The ether was evaporated and the residue partially crystallized to give 0.9 g of oily solid and 0.6 g of yellow oil. The solid was recrystallized four times from pentane to give 0.28 g of **6**, mp 75–77°.

5,9-Di-*t*-butylspiro[*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one-10,2′-[1′,3′]dioxolane] (7). A mixture of 0.6 g of **4**, 1 ml of ethylene glycol, 100 mg of *p*-toluenesulfonic acid, and 10 ml of benzene was refluxed for 2 hr under a Dean–Starke trap. Acetone (5 ml) was added to exchange selectively any diketal that might have formed. The mixture was then poured into 50 ml of water. The benzene layer was separated and the aqueous layer was extracted with ether. The ether extracts and the benzene extract were combined, washed with water, and dried. Distillation of the solvent at atmospheric pressure left an oily residue that was crystallized from pentane to give 0.3 g of solid, mp 95–98°. One recrystallization gave **7**, mp 94–95°.

2,4-Di-*t*-butylcyclopentanone Ethylene Ketal (15). A mixture of 500 g of 3,5-di-*t*-butylphenol and 50 g of Raney nickel (W-2) was placed in a 2-l. rocking autoclave and charged with hydrogen to 2300 psig. The mixture was heated to 200° and the pressure was maintained near 2000 psig for 3 days. The bomb was then cooled and the solid product was distilled from the Raney nickel to give 415 g (83%) of a mixture of stereoisomeric 3,5-di-*t*-butylcyclohexanols.

The mixture of cyclohexanols (210 g, 0.99 mole) was added to a vigorously stirred solution of 0.5 g of vanadium pentoxide in 800 ml of 50% nitric acid over a period of 8 hr. The temperature was maintained at 60–65° by means of gentle heating when necessary. After addition was complete, the mixture was stirred for 2 hr at 65° and then cooled to 10° in an ice bath. The aqueous acid was decanted. The remaining gummy solid was washed with water and then taken up in 150 ml of ethanol. The ethanolic solution was cooled to 10° and the precipitate was collected on a suction filter, washed with cold ethanol, and air dried to give 90 g (35%) of 2,4-di-*t*-butyladipic acid, mp 173–178°. The mother liquors and washings were steam distilled to remove excess ethanol. The residue was taken up in dilute sodium hydroxide and the resulting solution washed with ether. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether. The ether extract was dried. Evaporation of the ether left a residue that was crystallized twice from ethanol to give an additional 15 g (total yield of 41%) of the adipic acid, mp 174–178°. An analytical sample of 2,4-di-*t*-butyladipic acid was prepared from the crude product by recrystallization from methanol and melted at 178–179°.

Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.08; H, 10.14; NE, 129. Found: C, 65.36; H, 10.31; NE, 129.

A mixture of 69 g of 2,4-di-*t*-butyladipic acid and 1.5 g of barium hydroxide was heated to 290° in a Wood's metal bath. The yellow oil which distilled out of the mixture was dried over magnesium sulfate and redistilled to give 38 g (74%) of 2,4-di-*t*-butylcyclopentanone, bp 95–97° (3.6 mm).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 80.03; H, 12.62.

A mixture of 28.4 g (0.145 mole) of 2,4-di-*t*-butylcyclopentanone, 46.5 g (0.314 mole) of ethyl orthoformate, 1.5 g of *p*-toluenesulfonic acid, and 155 ml of ethylene glycol was stirred for 36 hr at room temperature. A 20% aqueous sodium hydroxide solution (10 ml) was added and the upper layer was separated. The lower layer was diluted with an equal volume of water and extracted with two 50-ml portions of ether. The ether extracts were combined with the upper layer, washed with dilute sodium hydroxide solution, and dried over sodium bicarbonate. The ether was evaporated and the residue distilled to give 31.6 g (91%) of **15**: bp 55–60° (0.05 mm); $n^{25}\mathrm{D}$ 1.4609.

2,4-Di-*t*-butyl-4-bromo-2-cyclopentenone (16) and 3,5-Di-*t*-butyl-5-bromo-2-cyclopentenone (17). Bromine (26.7 g, 0.167 mole) was added to a solution of 20 g (0.0835 mole) of **15** in 100 ml of ether as rapidly as the color of the bromine was discharged. The ether was allowed to reflux. When the addition was complete, 20 ml of water was added slowly. The ether was evaporated under vacuum and the residue was distilled at a pressure of 0.05 mm. The distillate was cut arbitrarily into three fractions: the first of these was taken from 80–90° (7.4 g), the second was taken from 90–95° (3.5 g), and the third was taken from 95–100° (5.6 g).

The first fraction was crystallized from pentane to give 2.6 g of material, mp 88–92°. The second was crystallized twice from pentane to give 0.9 g of material, mp 90–93°. These two crops were combined and crystallized once from pentane to give 2.6 g (8.7%) of **16**, mp 91–94°.

The third fraction was recrystallized from pentane to give a solid, mp 65–75°. Repeated recrystallization failed to alter the melting point. The combined mother liquors from the other fractions gave a similar material on crystallization from pentane. The material was a mixture of **16** and **17** as determined from its nmr spectrum.

The pot residue from the distillation gave 0.3 g of **17**, mp 94–

101°, after crystallization from pentane. Repeated recrystallizations from pentane gave white needles, mp 100–101°.

2,4-Di-*t*-butylcyclopentadienone (18). A mixture of 50 mg (0.183 mole) of **16** and 1.0 ml of triethylamine was left at room temperature for 15 min. The resulting slurry was mixed with 10 ml of water and extracted with 10 ml of pentane. The pentane extract was washed with 10% sodium hydrogen sulfate solution and 10% sodium bicarbonate solution and dried over magnesium sulfate. The pentane was evaporated in a stream of nitrogen and the residue was sublimed at 0.1 mm and room temperature to give 20 mg (57%) of **18** which melted at 30–31°.

3,5-Di-*t*-butyl-1,2,3,6-tetrahydrophthalic Anhydride (19). A mixture of 50 g (0.50 mole) of pinacolone, 12 g (0.30 mole) of sodium amide, and 100 ml of benzene was refluxed on the steam bath overnight, during which time a solid mass of material was formed. Acetic acid (25 ml, 0.41 mole) was added to the cooled mixture, whereupon the mixture came to reflux. The benzene solution was washed with water and dried over magnesium sulfate. The benzene was removed by distillation and the residue was distilled at reduced pressure to give 37.4 g (90%) of 2,2,5,6,6-pentamethylhepten-3-one, bp 43–45° (0.25 mm).

A solution of 30.0 g (0.165 mole) of 2,2,5,6,6-pentamethylhepten-3-one in 100 ml of anhydrous ether was added dropwise to a stirred suspension of 2.8 g (0.072 mole) of lithium aluminum hydride in 100 ml of anhydrous ether. The resulting mixture was stirred for 0.5 hr and then 20 ml of saturated ammonium chloride was added slowly. The ether solution was decanted from the resulting solid, which was then washed with ether. The ether was evaporated from the combined ethereal solutions. The residue, 29.0 g (97%) of viscous oil having n^{25}D 1.4510, was pure 2,2,5,6,6-pentamethyl-4-hepten-3-ol, as judged by its nmr spectrum.

The crude carbinol was dissolved in 150 ml of benzene and a few crystals of iodine were added. The mixture was refluxed under a Dean–Starke trap for 15 hr, at which time 2 ml of water had been removed. The benzene solution was washed with sodium thiosulfate solution and then dried over magnesium sulfate. The benzene was removed by distillation at atmospheric pressure and the residue was distilled to give 17.6 g (66%) of 2-*t*-butyl-5,5-dimethyl-1,3-hexadiene, bp 87–89° (50 mm) [lit.[20] bp 59–61° (15 mm)].

A mixture of 10.0 g (0.0602 mole) of the diene and 5.9 g (0.0602 mole) of maleic anhydride in 50 ml of anhydrous ether was left at room temperature for 24 hr. The mixture was cooled in an ice bath and the product was collected on a suction filter and air dried to give 11.4 g of crude **19**, mp 130–132° (lit.[20] mp 129°). Concentrating and cooling the mother liquors gave a second crop of 1.6 g of **19**, mp 128–132°, for a total yield of 82%.

3,5-Di-*t*-butylphthalic Anhydride (20). A mixture of 8.0 g (0.030 mole) of **19** and 2.4 g (0.075 mole) of sulfur was heated to 250° for 2 hr, when hydrogen sulfide evolution ceased. The mixture was cooled and 6 ml of 30% sodium hydroxide solution was added. Sodium carbonate (5 g) was added to the mixture and the paste was pressed dry and washed with carbon disulfide. The crude acid was liberated with concentrated hydrochloric acid and collected by filtration. The crude acid was taken up in 5% sodium bicarbonate solution, treated with active carbon, filtered, liberated with dilute hydrochloric acid, and collected by filtration The solid was again taken up in 5% sodium bicarbonate solution and then treated with 5 ml of 30% hydrogen peroxide in order to remove traces of sulfur. The acid was liberated with dilute hydrochloric acid, collected, and air dried to give 4.5 g (53%) of 3,5-di-*t*-butylphthalic acid.

A 2.0-g portion of the acid was heated in a vacuum sublimator at 160° (0.1 mm) for 1 hr. The sublimate was resublimed at 130° (0.1 mm) to give 1.0 g (53%) of **20**, mp 88–91°. One recrystallization from pentane gave 0.9 g of **20**, mp 93–94°.

Synthesis of 20 from 18. Crude **18** was prepared from 250 mg (0.9 mole) of **16** as described previously and mixed with 1.0 cc of dimethylacetylene dicarboxylate. The gas which was evolved was collected at constant pressure. At the end of 3 hr, gas evolution had ceased and the yellow color of the solution had faded. A total of 0.71 mmole of gas was evolved. When this gas was bubbled through Tollen's reagent, a black precipitate formed. The excess dimethylacetylene dicarboxylate was distilled at reduced pressure and the residue was refluxed with a 10% solution of sodium hydroxide in ethanol for 0.5 hr. Most of the ethanol was removed by distillation and the residue was then taken up in water. The aqueous solution was washed with ether, acidified with hydrochloric acid, and extracted with ether. The extract was dried and the ether was distilled. The residue was sublimed at 160° (0.1 mm) to give 153 mg (58%) of a glassy oil. Chromatography of the oil on 10 g of silica gel slurry packed in a 12-mm column gave 45 mg (17%) of a solid, mp 77–90°, after eluting with 200 ml of petroleum ether (bp 60–80°) followed by 100-ml portions of 5–50% benzene in petroleum ether in 5% steps. The solid was collected in the 20 and 25% benzene fractions. Two recrystallizations of the solid from pentane gave 23 mg of a solid, mp 93–94°. A mixture melting point with a sample of **20** obtained from **19** was undepressed. The infrared spectrum of the solid was identical with that of **20** obtained from **19**.

1,4,6,8-Tetra-*t*-butyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione (21). Crude **18** (81 mg) was prepared as described previously and then allowed to dimerize at room temperature. After 2 days the material had decolorized. It was sublimed at 100° (0.2 mm). The first 10 mg of sublimate was discarded. The remainder of the sublimate (70 mg, 80%) was pure **21**, mp 151–153°.

3-*t*-Butyl-1-N,N-dimethylaminocyclopentane (22). A solution of 155 g of 3-*t*-butylcyclopentanone[54] in 360 ml of 90% formic acid was added dropwise to a refluxing solution of 60 g of 90% formic acid in 200 g of N,N-dimethylformamide over a period of 1.5 hr. Water and formic acid were then allowed to distil out of the mixture while the temperature was raised to 200°. The resulting mixture was refluxed for 1.5 hr, then cooled to room temperature. A 50% aqueous solution of sodium hydroxide (400 g) was added cautiously. Water (100 ml) was added to dissolve the salts and the organic layer was separated, dried over sodium hydroxide, and distilled to give 108 g (58%) of **22**, bp 42° (0.3 mm).

1-*t*-Butylcyclopentene (23). To a stirred solution of 108 g (0.64 mole) of **22** in 200 ml of isopropyl alcohol, 91 g of methyl iodide was added in one portion. A vigorous reaction ensued and the mixture refluxed. When the mixture had cooled to room temperature, the product was collected by filtration. A second crop of product was obtained on cooling the mother liquor in an ice bath. The combined crops of methiodide were air dried and dissolved in 200 ml of water. Moist silver oxide, freshly prepared from 119 g of silver nitrate, was added to the solution. The mixture was stirred until the aqueous phase gave a negative test for iodide ion. The mixture was filtered and the precipitate was washed with hot water. The combined filtrates were concentrated by distillation and the residue was pyrolyzed at atmospheric pressure. The olefinic distillate was washed with 10% aqueous hydrochloric acid until the washes were acidic and then with 10% aqueous bicarbonate until the washes were basic. The olefin was dried over magnesium sulfate and distilled to give 36.5 g (51%) of a mixture of 3- and 4-*t*-butylcyclopentenes.

Lithium (1 g, 0.14 g-atom) was stirred with 100 ml of ethylenediamine under a nitrogen atmosphere until the deep blue color of dissolved lithium was discharged.[22] The mixture was heated to 120° and 25.0 g (0.202 mole) of the *t*-butylcyclopentenes was added. The mixture was refluxed for 3 days. Samples were withdrawn periodically and analyzed for **23** by nmr. When analysis showed more than 92% **23**, 15 ml of water was added to the cooled mixture. The resulting mixture was then poured onto 100 ml of water. The organic layer was separated and the aqueous layer was extracted with pentane. The extract and organic layer were combined and washed with water, dried, and distilled at atmospheric pressure to give 16.8 g (67%) of **23**, bp 137–139° (740 mm).

2-*t*-Butyl-2-cyclopentenone (24). A solution of 12.4 g (0.10 mole) of **23** in 20 ml of ethanol was cooled to −10°. Ethyl nitrite was prepared[55] from 19 g of sodium nitrite and condensed into the ethanolic solution. Water (2.0 ml) was added to the mixture, then gaseous hydrochloric acid from a cylinder was slowly bubbled into the mixture at a rate such that the temperature of the mixture did not rise above −10°. When the mixture set up into a stiff paste, addition of hydrochloric acid was stopped. The mixture was allowed to stand for 0.5 hr. Then the solid nitrosyl chloride adduct was collected by filtration with the aid of small portions of cold ethanol.

Pyridine (20.0 ml) was added slowly to the moist adduct at such a rate that the temperature of the mixture remained less than 80°. The mixture was heated on the steam bath for 1 hr and then poured into 200 ml of water. The precipitate was collected by filtration, air dried, and recrystallized from 50 ml of 60% ethanol to give 10.4 g (68%) of oxime of 2-*t*-butyl-2-cyclopentenone, mp 122–123°.

Anal. Calcd for $C_9H_{15}ON$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.37; H, 9.61; N, 9.09.

A solution of 10.0 g (0.0654 mole) of oxime in 50 ml of 16% hydrochloric acid was heated on the steam bath for 1 hr. The resulting mixture was cooled and extracted with three portions of

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(55) E. E. Royals and S. E. Horne, Jr., *J. Amer. Chem. Soc.*, 73, 5856 (1951).

pentane. The pentane extracts were combined and dried over magnesium sulfate. The pentane was evaporated and the residue distilled to give 6.7 g (74%) of **24**, bp 75° (10 mm).

4-Bromo-2-butyl-2-cyclopentenone (25). A mixture of 3.00 g (0.0217 mole) of **24**, 3.19 g (0.0217 mole) of N-bromosuccinimide, 0.10 g of benzoyl peroxide, and 30 ml of carbon tetrachloride was refluxed for 1 hr. The mixture then was washed with water and aqueous sodium thiosulfate, and finally dried. The solvent was evaporated under vacuum and the residue distilled. After a forerun of 0.6 g, a center cut of 2.2 g (47%) of pure **25** was collected, bp 75° (1.0 mm). A pot residue of 1.1 g was saved. Analysis by nmr showed that the forerun contained 29% **24**, in addition to **25**, and that the pot residue contained 8.5% of another compound. In a run using an 8.0% excess of NBS, the distilled product contained 11.6% of this compound. The presence, in the nmr spectrum of the mixture, of sharp singlets at τ 2.54 and 6.47 in a relative area of 1:2, in addition to a *t*-butyl resonance at τ 8.19 suggests that the compound is 4,4-dibromo-2-*t*-butyl-2-cyclopentenone.

***endo*-4,4-Di-*t*-butyltricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dione (27).** A solution of 0.20 g of **25** in 2.0 ml of triethylamine was allowed to stand for 0.5 hr. The resulting paste was taken up in pentane and water. The pentane solution was washed with 10% aqueous sulfuric acid and water, and dried. The pentane was evaporated to give 0.14 g (100%) of white solid, mp 134–140°. An analytical sample, prepared by recrystallization from pentane, melted at 141–143° dec.

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Organometallic Electrochemistry. XV.[1] Electron–Nuclear Spin–Spin Coupling Involving Mercury. Organomercurial Radical Anions

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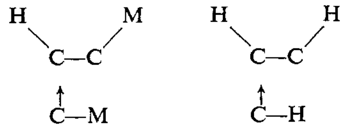
Abstract: A series of organomercurial radical anions have been prepared, and hyperfine splitting constants for mercury, a_{Hg}, measured. It appears that a McConnell-type equation holds: $a = Q_{HgC}{}^{Hg}\rho_C$, with $Q_{HgC}{}^{Hg} \cong -200$ G.

Simple consideration of the Fermi contact interactions which are the heart of the electron–nuclear coupling in the esr experiment and the nuclear–nuclear coupling in the nmr experiment suggest that it would be of interest to take two systems and measure the indicated parameters, comparing these with optical hyperfine structure constants, which derive from spectroscopic studies on H and M, and which were first explained by Fermi using the contact interaction which now bears his name.



J_{M-H} vs. J_{H-H} a_M vs. a_H

Hydrogen is a natural choice as one of the nuclei because of its low electronegativity and rather straightforward bonding to carbon, which is well understood theoretically. The choice of a comparison nucleus is rather more difficult, and preliminary work on organoboron and organophosphorus systems has uncovered rather formidable synthetic and theoretical barriers. This paper therefore focuses on a series of stable organomercurial radical anions, and compares the observed electron–nuclear coupling with the available literature data to make the suggested juxtaposition.[2,3]

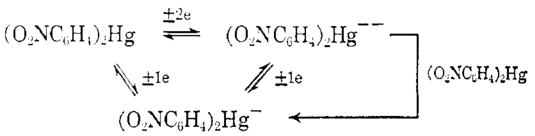
Results

It has been previously reported[4] that diphenylmercury reduces at a mercury cathode in a two-electron step to yield two phenyl anions and mercury metal.

$$(C_6H_5)_2Hg \xrightarrow[-3.2\ V]{2e} 2C_6H_5{:}^- + Hg \qquad (1)$$

The low bond strength of carbon-mercury linkages and the high negative charge at carbon in the presumed anion intermediate are together presumably responsible for the cleavage. Attempts to reduce spin density at the C–Hg site and to stabilize the anion intermediates by means of naphthyl or biphenyl groups failed. However, mono- and bis(nitroaryl)mercury compounds reduce to yield radical species.

When bis(*p*-nitrophenyl)mercury is reduced in dimethoxyethane, employing tetrabutylammonium perchlorate as a supporting electrolyte, there seems little doubt that the system can be represented as



(2)

The following observations were made. (1) The compound exhibited a well-defined polarographic wave at −1.84 V *vs.* 10^{-3} *M* Ag^+–Ag . (2) Triangular voltammetry at 1 V/sec sweep speeds showed an *i*/*e* plot characteristic of an electrochemically reversible process. (3) Controlled potential reduction at −2.0 V gave a

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[1] For previous papers in this series see R. E. Dessy, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4963 (1969).

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[4] R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *J. Amer. Chem. Soc.*, **88**, 460 (1966).