

This hypothesis (c) requires much further testing before it can be accepted, but it is consistent with the information so far available concerning the rates of hydrolyses of phosphate, phosphonate, and phosphinate esters. It may further account for the accelerated hydrolyses of strained silicon compounds.¹²

Methyl propylphosphonate was synthesized by the method previously³ used for ethyl propylphosphonate; its composition was established by high-resolution mass spectrometry and its structure by nmr spectroscopy. Rates of hydrolysis were measured by following the appearance of the nmr singlet for the methyl group of methanol; the chemical shift for this peak differs appreciably from that for the doublet from the methyl group of methyl propylphosphonate.

(12) L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, *J. Am. Chem. Soc.*, **79**, 3295 (1957); L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

Edward A. Dennis, F. H. Westheimer

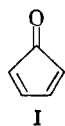
James Bryant Conant Laboratory of the Department of Chemistry
Harvard University, Cambridge, Massachusetts

Received June 3, 1966

2,4-Di-*t*-butyl- and 3-*t*-Butylcyclopentadienones

Sir:

Cyclopentadienone (**1**) is recognized as being unusually reactive toward normal Diels-Alder dimerization and numerous efforts to isolate it have been unsuccessful.¹ The evidence that **1** may indeed exist as a metastable species derives from successful trapping experiments in which **1** was found to react largely, if not exclusively, as a dienophile.^{1b,c} Testimony to the pronounced reactivity of **1** is that, except for indenone and one further example (see below), only tri- and tetrasubstituted derivatives of **1** have been isolated as



monomers.¹ Krüerke and Hübel reported² the isolation of a crystalline (yellow) di-*t*-butyl-**1**; however, their characterization of this material was incomplete and no chemical or spectral properties of it were determined.

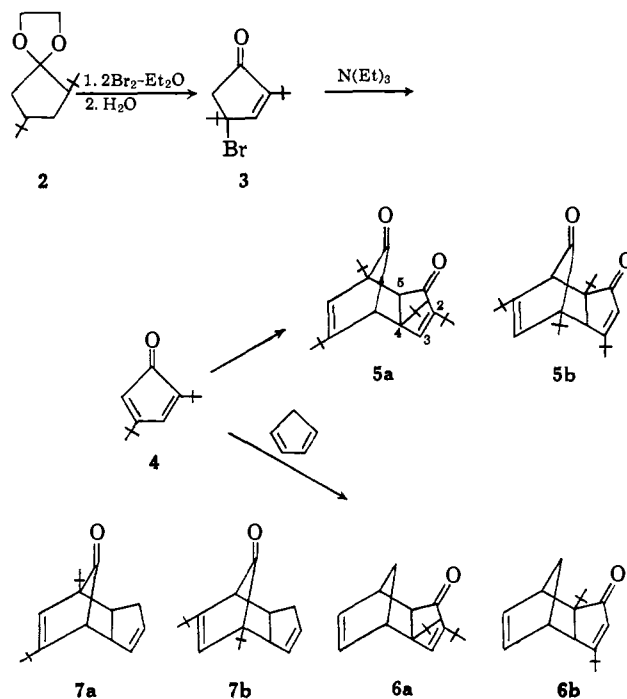
We have sought to probe the origin of the reactivity of **1** by attempting to acquire fundamental information from its simple derivatives whose dimerization reactions are sterically dissuaded yet whose π -electronic systems are relatively unperturbed. In this preliminary note we will describe the synthesis and spectral properties of 2,4-di-*t*-butyl- and 3-*t*-butylcyclopentadienones (**4** and **10**, respectively).

Nitric acid oxidation of a mixture of stereoisomeric 2,4-di-*t*-butylcyclohexanols led to 10–54% of 2,4-di-*t*-butyladipic acid, which was converted to 2,4-di-*t*-butylcyclopentanone (40%) upon pyrolysis with barium

(1) (a) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965); (b) K. Hafner and K. Goliash, *Chem. Ber.*, **94**, 2909 (1961); (c) C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964).

(2) U. Krüerke and W. Hübel, *Chem. Ber.*, **94**, 2829 (1961).

hydroxide at 290°. Ketalization of this ketone gave **2** (75%). Bromination (2 equiv) of **2** in ether followed by treatment with aqueous bicarbonate led to 18% (73% unisolated) of purified **3**, mp 80–83°; $\nu(\text{CCl}_4)$ 1700 (C=O) and 1603 cm^{-1} (C=C); $\tau(\text{CCl}_4)$ 8.85 and 8.80 (*t*-Bu), 7.07 (CH₂), and 2.77 (vinyl); all nmr absorptions are sharp singlets.³ The details of this bromination reaction are yet obscure. Treatment of **3** with neat



triethylamine led quantitatively to **4**, mp 30–31° (yellow). Dimerization of **4** proceeds slowly (see Table I) at 25° to give a single product which probably is either **5a** or **5b**, although two additional sterically more crowded *endo* adducts are possible. On the basis of the *single* vinyl and bridgehead proton resonances at τ 3.35 and 7.12, respectively, we feel that **5a** is most likely the product. Cyclopentadiene and **4** react at 25° more rapidly than the self-dimerization of **4** to give approximately an equal mixture (from nmr and infrared) of **6a** or **6b** and **7a** and/or **7b** (**4** reacts, in this instance, equally well as a diene and dienophile). The *single* vinyl proton resonance at τ 3.30 (spectrum taken of the mixture) is most compatible for **6a**, in which event this material comprises 50 mole % of the product. The spectral properties of **4**–**7** are summarized in Table I.

6,6-Dimethyl-2,5-heptanedione was converted to **8** (30%) by high dilution reaction with sodium amide in refluxing benzene. Bromination (NBS) of **8** led to 53% of **9**, mp 39–40°, $\nu(\text{CCl}_4)$ 1718 (C=O) and 1590

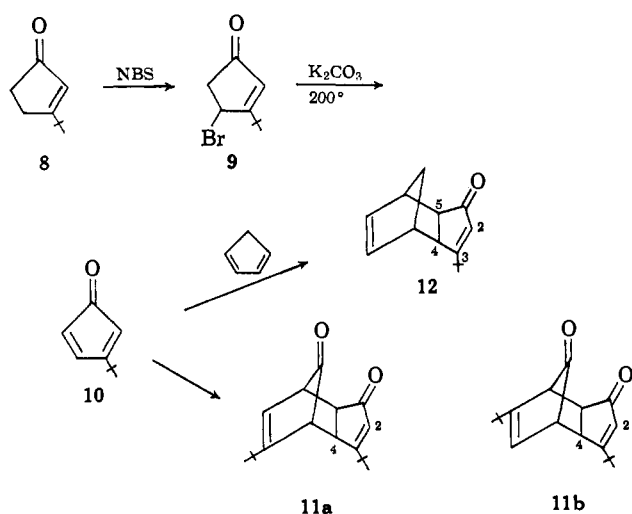
(3) **3** (mp 90–91°) may be obtained by repeated recrystallization from pentane. Bromination of the ketone of **2** gave predominantly 5-bromo-2,4-di-*t*-butylcyclopent-2-enone which did not dehydrobrominate readily with triethylamine. This bromide was obtained in minor quantities from the bromination of **2** and was difficultly removed from **3**.⁴ A second isomer of **3** (mp 100–101°) was isolated from bromination of **2**. Spectral and analytical data indicate that it is 5-bromo-3,5-di-*t*-butylcyclopent-2-enone.

(4) The microanalytical C and H percentages on all of the stable compounds reported were in agreement with expectation within ± 0.3 . Samples of dienone **4** gave percentages that were slightly below this limit due to trace contamination by 5-bromo-2,4-di-*t*-butylcyclopent-2-enone (by nmr)³ which cosublimed with **4** upon purification.

Table I. Spectral Data

Compd	Solvent	Ultraviolet ^a				Nmr, ^b τ						$\nu_{C=O}$, cm ⁻¹ ^b	<i>k</i> , l. mole ⁻¹ sec ⁻¹ (dimerization)
		λ_{max} , m μ	log ϵ	λ_{max} , m μ	log ϵ	H ₂	H ₃	H ₄	H ₅	<i>t</i> -Bu	Other		
4	EtOH	217	3.87	395	2.36		3.50		5.07	8.83	$J_{3,5} = 1.7$ Hz	1708	2.4×10^{-5} (25°)
	<i>i</i> -C ₈ H ₁₈	210 ^c	3.86	390	2.43								
5a ^d	Vapor	209	...	385	...								
	MeOH ^e	203	3.88	231	3.80		3.35		7.12		τ 4.13 (doublet)	1700	
6a ^d	<i>i</i> -C ₈ H ₁₈ ^f	193	4.12	226	3.80	...	3.30 ^g	τ 6.88 (doublet)	1765	10^2 (-20°)
												1695 ^h	
7 ^d												1765 ^h	
10	MeOH ^h	210	<i>i</i>	375	<i>i</i>								
	<i>i</i> -C ₈ H ₁₈ ^h	200	4.71	Ca. 380	>1.9								
11 ^d	MeOH ⁱ	202	3.94	231	4.04	4.00	8.78	$J_{2,4} = 1.0$ Hz	1710	
	<i>i</i> -C ₈ H ₁₈ ^k	197	4.14	223	4.00					9.00		1790	
12 ^d	MeOH ^l	201	3.73	233	4.07	4.37	...	6.62	7.28	8.82	$J_{2,4} \sim 1$ Hz	1698	
	<i>i</i> -C ₈ H ₁₈ ^m	193	3.88	225	4.02								

^a λ_{max} values reliable to ± 3 m μ due to broadness of bands. ^b In CCl₄. ^c Broad band <195 to 220 m μ . ^d The adducts are presumed to be *endo*. ^e $\lambda_{max}^{n \rightarrow \pi^*}$ 334 m μ (log ϵ 1.96). ^f $\lambda_{max}^{n \rightarrow \pi^*}$ 337 m μ (log ϵ 1.91). ^g Taken of a 1:1 mixture of 6 and 7. ^h At -60. ⁱ 10 dimerizes more rapidly in methanol than in *i*-C₈H₁₈ and an estimation of ϵ values was not possible. ^j $\lambda_{max}^{n \rightarrow \pi^*}$ 312 m μ (log ϵ 1.89). ^k $\lambda_{max}^{n \rightarrow \pi^*}$ 343 m μ (log ϵ 1.71). ^l $\lambda_{max}^{n \rightarrow \pi^*}$ 309 m μ (log ϵ 1.81). ^m $\lambda_{max}^{n \rightarrow \pi^*}$ 331 m μ (log ϵ 1.64).



cm⁻¹ (C=C); τ (CCl₄) 8.65 (*t*-Bu), 3.88 (H₂), 4.80 (H₄), 6.50 (H_{5a}), 7.42 (H_{5b}); $J = 19.3$ (5a,5b), 5.5 (4,5a), and 2.0 hertz (4,5b); H₂ is a singlet. Nitrogen (7 ml/min, STP) was passed through 9 (held at 65°) and then through a vertical potassium carbonate bed (20–40 mesh) maintained at 200°. The system pressure was 1–2 mm and the optimum delivery rate of 9 is about 20 mg/hr. The effluent was passed into a collection tube immersed in liquid nitrogen. Yellow 10 deposited on the walls of the tube. Injection of cyclopentadiene into the tube after stopping the nitrogen flow, followed by warming to ambient temperature, led to a rapid decolorization and production of ca. 50% 11 and 50% 12. Both 11 and 12 were synthesized from the ethylene ketal of 10 obtained by a sequence of reactions that will be described in our complete report. Crude 11 appears essentially homogeneous; however, a distinction between 11a and 11b has not yet been made. The minimum percentage of 10 initially collected was determined to be 92% by directing the effluent of a pyrolysis run onto 50 ml of stirred cyclopentadiene for 2.5 hr at -80° and analyzing the product for 11 and 12. Numerous attempts to obtain crude nmr data for 10 by collecting it at the orifice of an nmr tube at -196°, washing the sample into the tube with a jet of CDCl₃-CCl₄ (1:1), and instantly freezing, then warming the

sample rapidly to -80°, and rapidly scanning (both absorption and integral modes in separate experiments) the τ 1–5 region at -75° gave only the spectrum of 11 (operation time at -75 to -80° < 30 sec). For the ultraviolet spectra of 10: (a) 10 was collected in solvent (stirred) at -80° for 5–15 min (giving a 10⁻⁴ to 10⁻⁵ M solution) followed by rapid transfer to a precooled cell in the spectrometer held at -60°. At ca. 10⁻⁵ M 10 in isooctane, there was no change in absorbance of the 200-m μ band during 15 min. Consequently, the minimum initial amounts of 10:11 were ca. 11.5:1. (b) 10 was collected at -196° for ca. 1 hr, followed by addition of solvent (to give approximately a 10⁻³ M solution) and transfer to the spectrometer, as above. The 390-m μ band was scanned repeatedly; however, the relatively rapid dimerization at this concentration and temperature precluded our obtaining reliable extinction coefficients.

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

Acknowledgment. We are grateful for partial support of this work by the National Science Foundation (Grant No. G.P. 3589) and a generous unrestricted grant from Eli Lilly and Company.

Edgar W. Garbisch, Jr.,⁵ Richard F. Sprecher⁶

(5) Alfred P. Sloan Foundation Research Fellow.

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

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

Received March 21, 1966

On the Origin of the Cyclopentadienone Reactivity

Sir:

The origin of the exceptional reactivity of cyclopentadienone (1) to undergo the Diels–Alder dimerization is not known. There have been, however, numerous speculations on this matter. The ones most frequently encountered, perhaps because of their being intuitively attractive and reasonable *a posteriori*, are: (a) 1c may be uniquely unstable and may not contribute significantly to 1, thereby increasing the ground-state