

stituting eq 12 into eq 8. For the curves in Figure 8, eq 12 predicts that  $\tau_{\text{opt}}$  is  $1.5 \times 10^{-5}$  sec and  $I_{\text{peak}} = 2.5 \times 10 \times 10^{-7}f$ . Since the decay time of a molecule will be a constant for any given experimental condition, *i.e.*, it is difficult to adjust  $\tau$  to give  $\tau_{\text{opt}}$ , and since  $\tau_{\text{opt}}$  is a function of  $t_D$  and  $t_p$ , the maximum in the  $I$  vs.  $\tau$  curve can be made to occur at  $\tau_{\text{opt}}$  of any given sample (except a sample obeying eq 9) by adjusting  $t_D$  and  $t_p$ . For instance, if  $t_p$  is fixed, then the optimum value of  $t_D$ , *i.e.*,  $t_{D,\text{opt}}$ , may be found by solving eq 12 for  $t_D$ , and so

$$\tau_{D,\text{opt}} = t_p / \exp[(t_p/\tau) - 1] \quad (13)$$

The use of pulsing systems for time-resolved phosphorimetry seems to have many advantages over mechanical systems for analytical studies. It is hoped that commercial equipment to allow such measurements will soon be available.

**Current Measurement System.** The phototube output when using modulation or pulsing techniques can be measured using either an *integrating meter* or a *gated electronic system*. In the former, the average direct current signal from the photodetector is measured (the response time of the electrometer readout system is much longer than  $1/f$  of the mechanical or electronic chopper).

In the latter, the photodetector signal is *only* measured during the "on" time, *i.e.*, the photodetector output is only measured during time  $t_E$  when using a mechanical chopper (cross-hatched area in Figure 5) and during time  $t_p$  when using an electronic chopper (cross-hatched area in Figure 7). Since  $t_p \ll 1/f$  when using the gated system with electronic chopping, whereas  $t_E \sim 1/f = t_0$  when using the gated system with mechanical chopping, we would expect a considerable reduction of the dark current shot noise which is only measured during time  $t_p$ . In addition, by using pulsing techniques, it is possible to obtain about the same average power of luminescence radiation as when using modulation or continuous excitation techniques. Therefore a great improvement of the signal-to-noise ratio should result by using the gated system with electronic chopping or pulsing. In addition if photon counting techniques<sup>12</sup> are used, it is possible to discriminate against cosmic ray pulses, dynode chain pulses, leakage current, and stray pickup which further improves the signal-to-noise ratio.

*This research was supported by a grant from the U. S. Public Health Service (GM 11373-06).*

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## The Techniques of Flash Vacuum Pyrolysis. The Cyclopentadienyl Radical and Its Dimer

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The chemistry of organic free radicals, which are important reactive intermediates in numerous chemical reactions, has primarily been based on product and steady-state kinetic studies. Even though these indirect methods have led to an important and substantial body of information, it is often necessary and desirable to use more direct techniques. For example, the technique of flash photolysis, whereby radicals are generated photolytically by an intense flash of light and then immediately observed spectroscopically, has been very useful for the direct observation of radicals and of their elementary reactions. However, it is obviously limited to those radicals which can be generated photochemically. Flash vacuum pyrolysis (FVP) is an alternative and somewhat similar method which has special value for the study of thermal free radicals and related intermediates.

Flash vacuum pyrolysis is characterized by the use of low pressures and short contact times. The choice of these conditions has two important consequences. Because of the low pressures employed, typically in the range  $10^{-2}$  to  $10^{-4}$  torr, radical-molecule reactions in the oven are improbable with FVP. One can therefore study the primary pyrolytic intermediates uncompli-

cated by further chain or bimolecular radical-molecule reactions. The use of short contact times, generally in the range of 1 to 20 msec, permits a significant fraction of the radicals produced to survive the pyrolysis and emerge from the oven. Thus, FVP serves as a convenient and general method for generating free radicals or other reactive thermal intermediates for subsequent experiments.

The thermal fragments emerging from the oven can be studied by a variety of physical and chemical techniques. The pyrolysate may be passed directly into the ionization chamber of a mass spectrometer to obtain the mass and to establish the radical or molecule nature of a particular fragment. The fragment intensity as a function of the pyrolysis temperature (temperature profile) gives information about its ease of formation and stability. The only bimolecular processes usually observed under FVP conditions are radical-radical reactions which can also be studied mass spectrometrically. The ionization potentials of the fragments, when combined with the appropriate appearance potentials and thermochemical data, afford estimates of their heats of formation.

Detailed spectroscopic studies of the pyrolysis prod-

ucts may best be carried out by means of the matrix isolation technique. A rare gas is introduced at the tip of the pyrolysis oven where mixing occurs with the pyrolysate, and the whole is condensed on a rod or window in thermal contact with a liquid helium dewar. The dewars are fitted with the appropriate windows for determination of the optical spectra, or, alternatively, the matrix support rod can be lowered into a microwave cavity for the determination of the esr spectrum. Thus, the infrared, visible, ultraviolet, and esr spectra of the pyrolysate, which in most cases contains a significant fraction of normally unstable free-radical intermediates, can be obtained.

The chemical reactions of the emergent fragments are investigated by rapidly condensing these species on cold surfaces, usually at liquid nitrogen temperatures. The condensed fragments diffuse on the surface and ultimately couple or otherwise give products. Alternatively, the fragments may be condensed in a matrix. If diffusion occurs or is allowed to occur by warming the matrix, the fragments either couple or react with the matrix. Finally, the pyrolysate may be condensed on a surface coated with a reactive species of interest. In all cases reaction products are ultimately obtained by distillation from the cold surface to a vacuum manifold and can be analyzed by any of the usual techniques. Synthetically useful quantities of pyrolysis products are obtained by FVP in this way.

### Historical

A substantial body of previous work forms the basis for our experimental approach. The first demonstration that thermal free radicals have a discrete and measurable lifetime in the gas phase resulted from the classic metallic mirror experiments of Paneth and Rice.<sup>1</sup> A free-radical source such as acetone or tetramethyllead, diluted by a carrier gas, was passed through a hot quartz tube at 500–900° at low pressures (0.1–50 mm) and high linear velocities (1–10 m/sec). The radicals were detected by their reaction with metallic mirrors at varying distances from the hot zone. The removal of the mirror and the isolation of stable organometallic products constituted evidence for a particular free radical. Radicals detected in this way include methyl, ethyl, propyl, phenyl, and benzyl, using a wide variety of substances such as lead, zinc, beryllium, mercury, antimony, arsenic, bismuth, selenium, and iodine to form mirrors. Semiquantitative estimates of radical recombination rates or lifetimes were also obtained.

The first detection of a gas-phase free radical using mass spectroscopy was reported by Eltenton in 1942.<sup>2</sup> His work, which dealt with methyl radicals, laid the foundation for the extensive studies of both simple and complex organic free radicals carried out by Lossing and

coworkers.<sup>3</sup> This group studied over 70 organic free radicals and developed some of the techniques we now use. In addition, their data allow us to predict the reactions of a wide variety of organic molecules at FVP conditions. Other workers have reported significant mass spectral free-radical studies; this subject has been thoroughly reviewed.<sup>4</sup> Lossing<sup>5</sup> and Benson<sup>6</sup> recently have made progress in kinetic studies of thermal free radicals at low pressures using mass spectroscopy.

Recently a number of investigators have reported chemical studies on the high-temperature pyrolysis of organic molecules at reduced pressures in the gas phase.<sup>7</sup> The work of Skell<sup>8a,b</sup> is probably the most pertinent. Reactive thermal intermediates such as C<sub>1</sub> and C<sub>3</sub> were generated under high vacuum and allowed to react with olefins matrices at –196°. In addition, dichlorocarbene was generated at low pressures by decomposing chloroform over a tungsten filament or a perforated carbon disk at 1450°, and its reactions with butene matrices were studied.<sup>8c</sup>

The use of rare gas matrices for stabilization of simple radicals and high-temperature molecules is based on work initiated at the National Bureau of Standards.<sup>9</sup> Such matrices are formed at liquid helium or hydrogen temperatures and require the use of special dewars. The dewar systems used in our experiments were developed in our laboratory by Weltner and coworkers for their spectroscopic studies of high-temperature inorganic species (stellar intermediates).<sup>10,11</sup> Consequently it was relatively straightforward to apply these techniques to organic free radicals generated by FVP.

Thus many workers have contributed to the experimental techniques used in our present study. The unique feature of our effort is the combination of these techniques enabling a comprehensive investigation of the consequences of thermal activation of organic molecules and the properties of the resulting primary products.

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(4) A. G. Harrison in "Mass Spectroscopy of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 207.

(5) I. P. Fisher, J. B. Hoover, B. Roberts, and F. P. Lossing, *Can. J. Chem.*, **44**, 2205, 2211 (1966).

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(1) (a) F. Paneth and W. Hofeditz, *Ber.*, **62B**, 1335 (1929); (b) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Williams and Wilkins Company, Baltimore, Md., 1935; (c) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 100.

(2) G. C. Eltenton, *J. Chem. Phys.*, **10**, 403 (1942).

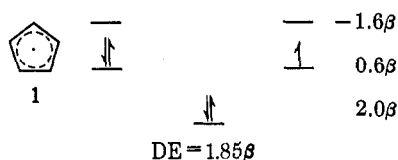


Figure 1. The cyclopentadienyl radical.

### The Cyclopentadienyl Radical

The results of our studies on the cyclopentadienyl radical (**1**) are discussed in order to illustrate the application of our techniques. This species has been the focus of a number of theoretical<sup>12</sup> and spectroscopic investigations,<sup>13</sup> even though its chemistry has not been explicitly explored.

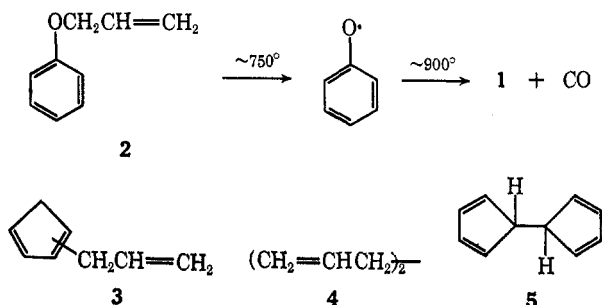
In terms of simple Hückel molecular orbital theory, the  $\pi$  molecular orbitals for fivefold symmetric **1** consist of a low-lying bonding molecular orbital and a higher pair of degenerate levels which are nearly non-bonding (Figure 1).<sup>12a</sup> Consequently, the radical is predicted to have some stability owing to its delocalization energy. A more rigorous treatment predicts that Jahn-Teller distortion should occur such that a twofold symmetric structure is about 2 kcal more stable than the fivefold symmetric structure.<sup>12b-d</sup> The ionization potential has been calculated by Streitwieser<sup>12e</sup> using his  $\omega$  technique. Finally, the lowest lying  $\pi$  excited state has been estimated to lie about 4 eV above the ground state.<sup>12f,g</sup>

Many of these predictions have been at least qualitatively confirmed. Lossing and coworkers first detected the cyclopentadienyl radical and a number of its substituted analogs by thermally decomposing phenyl ethers at low pressures at  $\sim 950^\circ$  in an oven coupled directly to the ionization source of a mass spectrometer.<sup>13a,b</sup> The measured ionization potential (8.6 eV) corresponded closely with that calculated.<sup>12e</sup> The esr spectrum of **1** has been reported by a number of investigators<sup>13c-f</sup> with the most comprehensive study being that of Liebling and McConnell.<sup>13f</sup> They irradiated a single cyclopentadiene crystal at low temperatures and found that the resulting esr spectrum was temperature dependent. At  $>70^\circ\text{K}$ , six lines were observed having a binomial distribution of intensities consistent with a fivefold symmetric species having a uniform spin distribution. However, at lower temperatures, the spec-

trum was more complex and was assigned to a distorted, twofold symmetric species, thus confirming the prediction of a Jahn-Teller distortion for **1**. Finally, the uv of **1** was observed by Porter and Ward<sup>13g,h</sup> when cyclopentadiene or a variety of benzene derivatives was flash photolyzed; the 0-0 band similarly was close to that predicted.<sup>12g,h</sup>

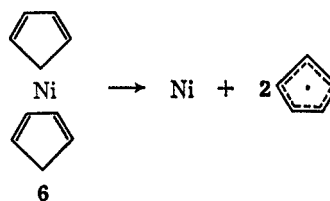
### Mass Spectroscopy

**Nickelocene as a Thermal Source of Cyclopentadienyl (1).** The ideal thermal cyclopentadienyl radical source should decompose to **1** in high yields, be readily available, and be easily handled. Lossing's work<sup>13a,b</sup> on the phenyl ethers suggested these molecules as potential candidates. In our investigation of the FVP of allyl phenyl ether (**2**)<sup>14</sup> we found that the major isolated reaction product after rapid quenching was allylcyclopentadiene (**3**) and biallyl (**4**). The cyclopentadienyl radical dimer (**5**), which is of substantial interest with respect to its dissociation, rearrangement, and cycloaddi-



tion reactions, was not detected. Furthermore, the complexity of the thermal fragmentation would make spectroscopic experiments difficult to interpret even though **1** is definitely a key intermediate.

Clearly, a molecular source which decomposes only to **1** without generating another radical fragment would be more useful. Earlier, Lossing noted<sup>13a</sup> that nickelocene (**6**) gave cyclopentadienyl radicals at  $950^\circ$  in his low-pressure thermal reactor. In order to obtain a firm basis for further experiments, we undertook a more detailed mass spectroscopic investigation of this pyrolysis.



Using the apparatus shown in Figure 2, we obtained the temperature profile shown in Figure 3.<sup>15</sup> As the parent molecule nickelocene thermally decomposed, three thermal products appeared:  $m/e$  65 ( $\text{C}_5\text{H}_5$ ), 130 ( $\text{C}_{10}\text{H}_{10}$ ), and 123 ( $\text{C}_5\text{H}_5\text{Ni}$ ). Cyclopentadiene ( $m/e$  66) was also obtained but is not shown. These products

(14) E. Hedaya and D. W. McNeil, *J. Am. Chem. Soc.*, **89**, 4213 (1967).

(15) P. Schissel, D. J. McAdoo, E. Hedaya, and D. W. McNeil, *J. Chem. Phys.*, **49**, 5061 (1968).

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 (13) (a) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960); (b) R. F. Pottier and F. P. Lossing, *ibid.*, **85**, 269 (1963); (c) S. Ohnishi and S. Nitta, *J. Chem. Phys.*, **39**, 2848 (1963); (d) P. Zandstra, *ibid.*, **40**, 612 (1964); (e) R. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964); (f) G. R. Liebling and H. M. McConnell, *J. Chem. Phys.*, **42**, 3931 (1965); (g) G. Porter and B. Ward, *Proc. Roy. Soc. (London)*, **A303**, 139 (1968); (h) G. Porter and B. Ward, *Proc. Chem. Soc.*, 288 (1964).

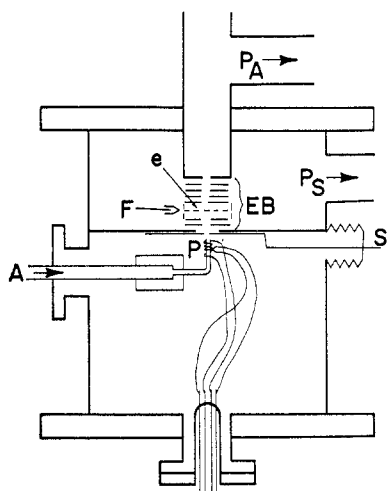


Figure 2. Electron bombardment source and pyrolysis oven: A, gas inlet; P, pyrolysis oven; S, shutter; F, electron bombardment filament; e, electron beam; EB, electron bombardment source; P<sub>S</sub>, source diffusion pump; P<sub>A</sub>, analyzer diffusion pump.

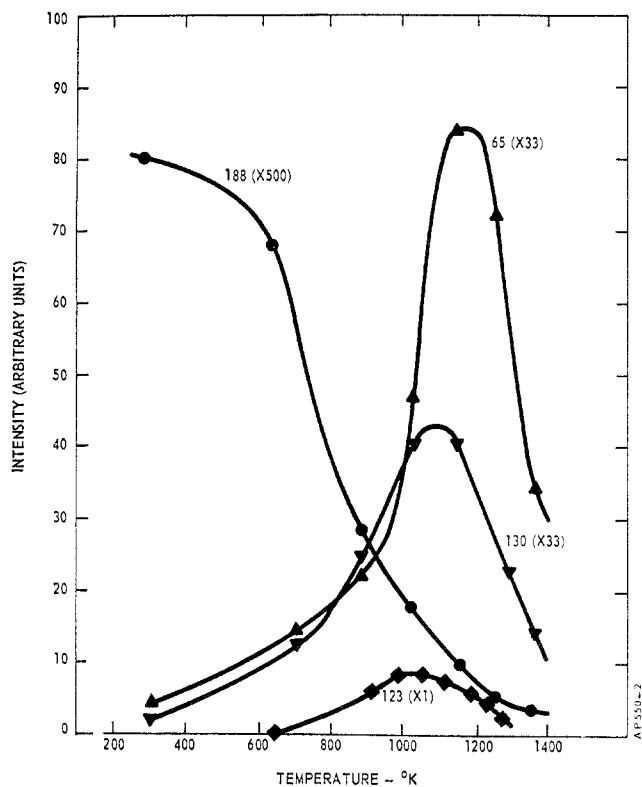


Figure 3. Nickelocene pyrolysis: ●, Ni(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>; ▲, C<sub>5</sub>H<sub>5</sub>; ▼, C<sub>10</sub>H<sub>10</sub>; ◆, NiC<sub>5</sub>H<sub>5</sub>. Electron bombardment spectrum with 11-eV electrons. Sensitivity attenuation factors noted.

were further characterized by their reactions with methyl or allyl radicals generated by the copyrolysis at low pressures of ethyl nitrite or allyl iodide, respectively, with nickelocene. The *m/e* 65 reacted with both methyl and allyl as evidenced by the appearance of peaks in the mass spectrum at *m/e* 80 and 106. In contrast, the species with *m/e* 123 did not react with methyl but did give a product with allyl at *m/e* 164, while C<sub>10</sub>-

Table I  
Ionization (IP) and Appearance (AP) Potentials

Species	IP, eV	Lit. IP, eV	AP, eV	Lit. AP, eV
Nickel		7.63 <sup>a</sup>	13.6	14.3 <sup>b</sup>
Nickelocene	6.8	7.06, <sup>b</sup> 6.75 <sup>c</sup>		
Cyclopentadienyl-nickel	7.8	9.3 (calcd) <sup>b</sup>	12.4	12.7, <sup>b</sup> 11.9 <sup>d</sup>
Cyclopentadienyl	8.56	8.69 <sup>e</sup>		
Dicyclopentadienyl	7.75			

<sup>a</sup> F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957. <sup>b</sup> L. Friedmann, A. P. Sousa, and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955). <sup>c</sup> A. Foffani, S. Pignataro, G. Distefano, and G. Immorta, *J. Organometal. Chem.*, **11**, 571 (1968). <sup>d</sup> S. Pignataro and F. P. Lossing, private communication. <sup>e</sup> Reference 13a.

H<sub>10</sub> did not react with either allyl or methyl. The ionization potentials were measured for these species along with some relevant appearance potential data (Table I).

These data constitute compelling evidence for the cyclopentadienyl radical in accordance with previous work.<sup>13a</sup> The new species at *m/e* 123 is best described as cyclopentadienylnickel on the basis of its low ionization potential close to that of nickel, its spectrum due to nickel isotopes, and its reactivity with allyl. The latter is especially significant since it is well known that nickel forms weak bonds to alkyl ligands but strong bonds to unsaturated ligands.<sup>16</sup> Although cyclopentadienylnickel is undoubtedly of theoretical and experimental interest, we have not been encouraged to study it further from nickelocene since it is formed in such low yields.

**Heterogeneity of the Nickelocene Pyrolysis.** The ionization and appearance potential measurements lead to estimates of dissociation energies *D*<sub>1</sub> and *D*<sub>2</sub> corresponding to gas-phase reactions 1 and 2. The values



obtained imply an endothermicity for these gas-phase reactions which is much too high for them to be important at the pyrolysis conditions used. Specifically, strong bonds such as those present in methane or benzene or even somewhat weaker bonds do not cleave at the conditions of the nickelocene pyrolysis. However, we can derive processes which are energetically more favorable by assuming that the fragmentation occurs on the reactor surface where nickel metal can be deposited. The high heat of vaporization of nickel (102 kcal)<sup>17</sup> then reduces the over-all endothermicity considerably. Consistently, we found that essentially all of the nickel from the decomposed nickelocene is deposited on the

(16) (a) C. F. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, Oxford, 1962; (b) G. Wilke and G. Herrmann, *Angew. Chem.*, **5**, 581 (1966); (c) G. Wilke, *Pure Appl. Chem.*, **17**, 179 (1968).

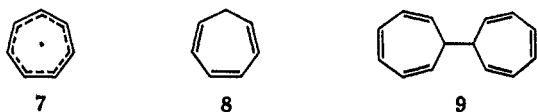
(17) R. Hultgreen, R. L. Orr, P. D. Anderson, and K. K. Kelly, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Department of Mineral Technology, University of California at Berkeley, Oct 1966.

walls of the oven. Finally, the difference  $D_1 - D_2$  leads to a  $D_3$  for dissociation of cyclopentadienylnickel which is about 35 kcal/mol. It is surprising, therefore, that we were able to detect this species.<sup>15</sup>

An important conclusion derived from these considerations is that both thermal activation and fragmentation can occur on hot reactor walls at low pressures. Clearly, *heterogeneous* surface reactions can lead to much more complex fragmentations compared to *homogeneous* unimolecular thermal fragmentations in the gas phase. Other examples of surface reactions during low-pressure pyrolysis studies have been noted.<sup>18</sup>

**The Heat of Formation of the Cyclopentadienyl Radical (1).** The stability of the cyclopentadienyl radical has been the subject of considerable theoretical discussion, and an estimate of its heat of formation ( $\Delta H_f(\text{Cp}\cdot)$ ) is of substantial interest. From  $D_1$  estimated above and the heats of formation of gaseous nickelocene and nickel, we estimate that  $\Delta H_f(\text{Cp}\cdot) \leq 58$  kcal/mol. Alternatively,  $\Delta H_f(\text{Cp}\cdot)$  can be estimated from the appearance potential of the cyclopentadienyl cation from cyclopentadiene:  $56 \pm 12$  kcal/mol.<sup>19</sup>

We can use  $\Delta H_f(\text{Cp}\cdot)$  to compare the thermodynamic properties of **1** and the tropenyl radical (**7**) which is a homologous monocyclic  $\pi$  radical. The dissociation of cyclopentadiene to **1** is endothermic by 78 kcal. The dissociation of 9,10-dihydrofulvalene (**5**) to **1** is similarly estimated as being endothermic by 40–45 kcal based on the heat of formation of **1** and that estimated for **5** by Benson's group equivalency values.<sup>20</sup> The endothermicities for dissociation of tropilidene (**8**) and ditropenyl (**9**) to tropenyl are correspondingly 73 and 35 kcal/mol, respectively.<sup>13a,21</sup> Consequently, the cyclopentadienyl and tropenyl radicals have closely similar stabilities compared to the hydride or dimer.



Simple Hückel molecular orbital theory predicts that tropenyl has  $0.4\beta$  more delocalization energy than cyclopentadienyl.<sup>12a</sup> However, the triene molecular source for the former is similarly predicted to be about  $0.4\beta$  more stable than the diene molecular source for the latter.<sup>12a</sup> The experimental stabilities are in reasonable agreement with simple theory provided that we account for differences in delocalization energies of the molecular sources.

### Matrix Isolation Spectroscopy

#### The ESR Spectrum of the Cyclopentadienyl Radical.

The esr spectrum of cyclopentadienyl, which was gen-

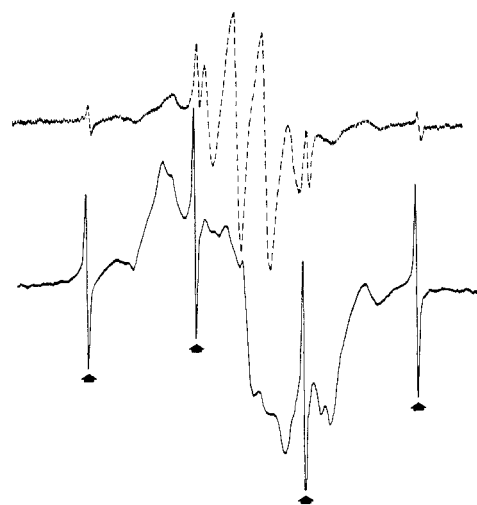


Figure 4. ESR spectra of the cyclopentadienyl radical in a neon matrix at 4°K (—) and ca. 12°K (---). Arrows indicate methyl radical signal.

erated by pyrolysis of nickelocene and which was isolated from the gas phase in a neon matrix,<sup>11</sup> is shown in Figure 4. Temperature-dependent spectra (Figure 4) were obtained by warming up the neon matrix, which was initially at or near 4°K, to ca. 12°K. The high- and low-temperature spectra are comparable with those previously obtained by Liebling and McConnell<sup>13f</sup> for cyclopentadienyl in a cyclopentadiene single crystal.

However, in our case the transition temperature between the two spectra was considerably lower than that observed in a cyclopentadiene crystal, indicating that the barrier for motion of the spin distribution in neon is lower than that in crystalline cyclopentadiene. Similarly, the barrier for inversion of the vinyl radical in neon was found to be considerably lower than that for vinyl in liquid ethane.<sup>22</sup> In the case of the cyclopentadienyl radical a molecular orbital calculation predicts a barrier of 1 to 27 cal/mol which closely corresponds to what must be the case in neon.<sup>12c,d</sup>

### Chemical Synthesis by FVP

**The Isolation and Characterization of 9,10-Dihydrofulvalene (5).** In the previous sections we have illustrated how a combination of FVP and certain spectroscopic techniques were used to characterize a transient intermediate. We believe, however, that one of the most significant but less appreciated aspects of FVP is its application to the synthesis of novel molecules using low-temperature rapid quenching. As an example, we shall discuss the synthesis and properties of 9,10-dihydrofulvalene (**5**) which is obtained most simply by the dimerization of **1**.

It is appropriate to describe past attempts to obtain **5**. Kealy and Pauson<sup>23</sup> attempted to oxidatively couple cyclopentadienylmagnesium bromide using ferric chloride. Instead, they obtained ferrocene and were

(18) T. P. Fehlner, *J. Am. Chem. Soc.*, **89**, 6477 (1967).

(19) (a) F. Dorman, *J. Chem. Phys.*, **43**, 3507 (1965); (b) H. S. Hull, A. F. Reid, and A. G. Turnbull, *Inorg. Chem.*, **6**, 805 (1967).

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(21) G. Vincow, H. J. Dauben, Jr., F. R. Huster, and W. V. Voland, *J. Am. Chem. Soc.*, **91**, 2823 (1969).

(22) (a) P. H. Kasai and E. B. Whipple, *J. Am. Chem. Soc.*, **89**, 1033 (1967); (b) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

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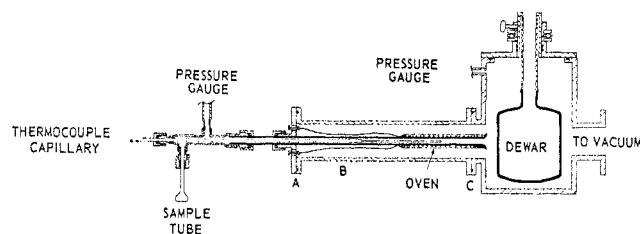
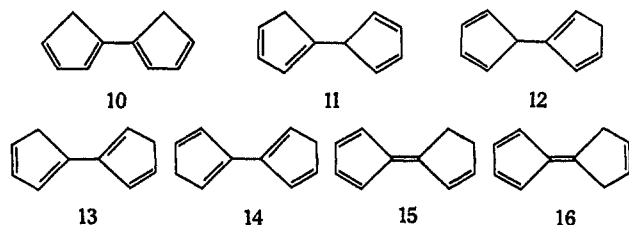


Figure 5. Flash vacuum pyrolysis apparatus for isolation of products.

diverted by this molecule's unique properties. Using a similar approach to ultimately synthesize fulvalene, Doering and Matzner<sup>24</sup> obtained a dilute air-sensitive solution of an isomer of **5**, 1,5-dihydrofulvalene (**10**), which they were unable to isolate. The structure was based on an intense uv maxima at 336  $\mu$  and reduction to the saturated hydrocarbon. A perchlorodihydrofulvalene has been prepared by a variety of methods.<sup>25</sup>

About 1 g of nickelocene was pyrolyzed in the apparatus shown in Figure 5 at about 0.08 Torr and 950°. Rapid quenching of the pyrolysate on the liquid nitrogen cooled dewar surface led to the isolation of three products: cyclopentadiene, naphthalene, and a liquid at 0°, which could be handled conveniently on a vacuum line but which rapidly polymerized in air or on standing *in vacuo* at 25°. A parent peak was observed at  $m/e$  130 for the latter and an ionization potential was obtained which was identical with that measured for  $m/e$  130 when nickelocene was pyrolyzed in the apparatus of Figure 2 (Table I).

Of the large number of  $C_{10}H_{10}$  isomers which are conceivable, we can list those which are most probable besides 9,10-dihydrofulvalene (**5**) and its isomer **10**.



We were able to assign the structure of the reactive product by using a combination of spectroscopy and chemistry. The nmr at low temperatures (Figure 6) first provides good evidence for structure **5** because of the vinyl proton resonance ( $\sim 6.5$  ppm) and the singlet at 3.2 ppm (area ratio 4:1). The symmetrical multiplet at 6.5 ppm changes to two complex multiplets and the singlet at 3.2 ppm becomes a quartet on warming to

(24) (a) W. von E. Doering in "Theoretical Organic Chemistry—The Kekule Symposium," Butterworths and Co. (Publishers) Ltd., London, 1959, p 45; (b) E. A. Matzner, Ph.D. Thesis, Yale University, 1958.

(25) (a) C. W. Roberts, D. H. Haigh, and W. G. Lloyd, *J. Phys. Chem.*, **64**, 1887 (1960); (b) A. Roedig and L. Horning, *Angew. Chem.*, **67**, 302 (1955); (c) E. L. McBee, J. D. Idol, Jr., and C. W. Roberts, *J. Am. Chem. Soc.*, **77**, 4375 (1955); (d) J. T. Rucker, U. S. Patent 2,908,723 (1959); (e) A. E. Ginsberg, R. Paatz, and F. Korti, *Tetrahedron Letters*, 779 (1962).

(26) E. Hedaya, D. W. McNeil, P. O. Schissel, and D. J. McAdoo, *J. Am. Chem. Soc.*, **90**, 5234 (1968).

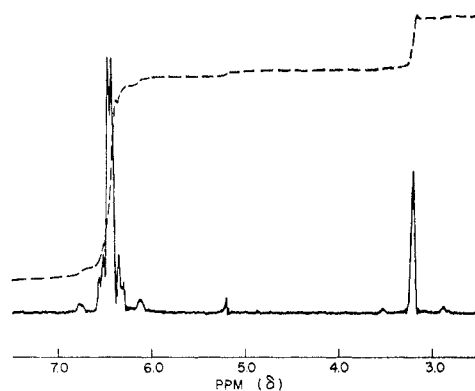
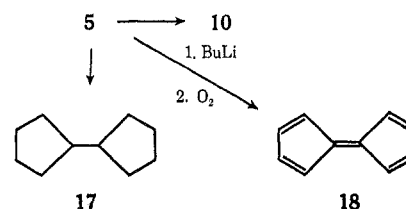


Figure 6. Nmr spectrum of 9,10-dihydrofulvalene at  $-10^\circ$ .

room temperature; the area ratio correspondingly increases to 3:2. We must now consider structures **10–16** as possible rearrangement products. However, we can rule out **15** on the basis of its reported nmr spectrum.<sup>27</sup>

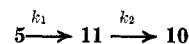
The corresponding uv spectra were obtained; **5** has a uv spectrum close to cyclopentadiene while that for the rearrangement product has an intense maxima at 336  $\mu$  ( $\epsilon \sim 14 \times 10^3$ ) and thus must be **10**.<sup>24</sup>

Chemical evidence for **5** and **10** was obtained by reduction to cyclopentanylcyclopentane (**17**) and oxidative dehydrogenation to fulvalene (**18**).<sup>24</sup>

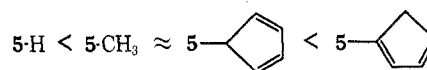


Since the rearrangement of **5** to **10** most likely involves an interesting series of sigmatropic hydrogen rearrangements,<sup>28</sup> a kinetic study was carried out. First-order rate constants ( $t_{1/2}$  (30.0°) 52.3 min) were obtained by uv in heptane which were independent of the initial concentration of **5**; activation parameters,  $\Delta H^\ddagger = 18.6$  kcal/mol and  $\Delta S^\ddagger = -16$  eu.

The rearrangement can be represented as two sequential 1,2 or 1,5 hydrogen shifts where **11** is an intermediate. Since good first-order rates were observed without buildup of **11**,  $k_1 \ll k_2$ .



This scheme implies that the rate of 1,5 hydrogen transfer depends upon the substituent at the migration origin. The limited data<sup>29</sup> for cyclopentadienes indicate that the relative rates of hydrogen transfer fall in the order



(27) K. V. Scherer, *ibid.*, **85**, 1550 (1963).

(28) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(29) (a) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965); (b) W. R. Roth, *Tetrahedron Letters*, **17**, 1009 (1964).

One striking inconsistency with the proposed scheme is the very negative entropy of activation. A 1,5 hydrogen shift in a planar cyclic diene should occur with little reorganization in the transition state and consequently should have  $\Delta S^\ddagger \approx 0$ . Actually, large negative entropies of activation for 1,5 hydrogen shifts have been noted for a number of other cyclic dienes such as 7-deuterio-,<sup>30</sup> 7-phenyl-,<sup>30</sup> and 7-methoxytropilidenes,<sup>31</sup> 1,4,6-cyclooctatriene,<sup>32</sup> and 1-deuterio-2,4-cyclooctadiene.<sup>33</sup> These can be rationalized as involving a lack of experimental precision in the kinetic measurements,<sup>34</sup> however, we believe this is unsatisfactory. Clearly, the simple scheme proposed above for **4** requires elaboration, and further studies are in progress.

One other interesting aspect of the 1,5 hydrogen shift in cyclopentadienes is its fast rate even though there is about a 50-kcal difference between the activation energy for rearrangement and the corresponding carbon-hydrogen bond dissociation energy. The enhanced rates of hydrogen migration for the cyclopentadienes can be ascribed to the unique closed cyclopentadienyl molecular orbital pattern which is developed in the transition state.

### Conclusion

In the above we have shown how a combination of techniques involving a common pyrolytic process can be

(30) A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Rec. Trav. Chim.*, **82**, 717 (1963).

(31) T. Nozoe and K. Takahashi, *Bull. Chem. Soc. Japan*, **38**, 665 (1965).

used to characterize directly a simple but relatively inaccessible reactive free radical. The information obtained encompasses thermodynamic, spectroscopic, and chemical properties. Although our primary purpose here is the illustration of the techniques of FVP by summarizing our work on one species (**1**), some of the other reactive intermediates or thermal processes currently being studied in our laboratory can be listed. These include cyclobutadiene<sup>35</sup> and its isomers, the thermal decarbonylation of phenoxy radicals<sup>34</sup> and a variety of related thermal rearrangements,<sup>36</sup> simple  $\pi$  radicals such as the benzyl radical,<sup>37</sup> and finally the synthesis and characterization of some "unusual" hydrocarbons.

*The work described here has involved a number of collaborators. The mass spectroscopic experiments were designed and carried out by Paul Schissel with the help of D. J. McAdoo and P. F. D'Angelo. The esr and optical spectroscopic experiments were carried out by P. H. Kasai, E. B. Whipple, C. L. Angell, and D. McLeod. In the early stages of our work, W. Weltner, Jr., offered helpful encouragement and advice. The chemical experiments were carried out by D. W. McNeil and M. E. Kent. Finally, F. P. Lossing has been especially helpful throughout our work particularly with respect to the interpretation of our mass spectral results.*

(32) W. R. Roth, *Ann.*, **671**, 25 (1964).

(33) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 999 (1968).

(34) K. Eggers, *J. Am. Chem. Soc.*, **89**, 3691 (1967).

(35) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *ibid.*, **91**, 1875 (1969).

(36) E. Hedaya, M. E. Kent, D. W. McNeil, F. P. Lossing, and T. McAllister, *Tetrahedron Letters*, **30**, 3415 (1968).

(37) C. L. Angell, E. Hedaya, and D. McLeod, Jr., *J. Am. Chem. Soc.*, **89**, 4214 (1967).

## Carbophosphoranes

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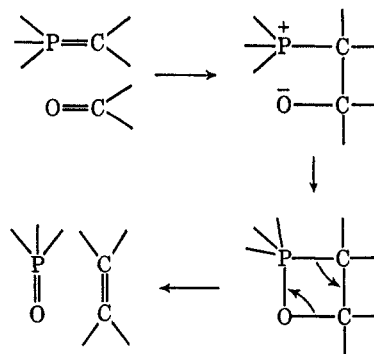
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Extensive research<sup>1-4</sup> on phosphonium ylides,  $(C_6H_5)_3P=CXY \leftrightarrow (C_6H_5)_3P^+-C^-XY$ , during the past 15 years has demonstrated broad synthetic utility resulting from their reactivity in the manner of carbanions and the ability of phosphorus to assume pentavalency and to form strong phosphorus-oxygen bonds. These characteristics are particularly evident in Wittig reactions<sup>1-4</sup> in which nucleophilic attack of such ylides on aldehydes or ketones yields olefins and triphenylphosphine oxide by way of acyclic betaines and four-membered-ring intermediates.



(1) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

(2) A. Maercker, *Org. Reactions*, **14**, 270 (1965).

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(4) S. Trippett, *Quart. Rev. (London)*, **17**, 406 (1963).

For the special case of phosphoranes having the general structure  $(C_6H_5)_3P=C=Z$ , heterocumulene reactivity is also significant. Research on such carbophos-