Cycloheptatrienyldiazomethane. Its Synthesis and Behavior. $C_{s}H_{s}$ Chemistry. X.¹ Correlation Diagrams and **Nodal Properties**

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Abstract: The synthesis of cycloheptatrienyldiazomethane is described, and the thermal and photochemical behavior of the compound is delineated. The nmr spectrum of the compound reveals that the cycloheptatrienyl valence tautomer is favored over the norcaradiene isomer. Cycloheptatrienyldiazomethane reacts with loss of nitrogen via three pathways. The first involves a cheletropic disengagement of acetylene from the norcaradiene valence tautomer of the carbene to leave benzene. The second reaction is a hydrogen migration to give heptafulvene. The last is a ring expansion to afford cyclooctatetraene. Although three a priori mechanisms are possible for the COT formation, the one involving bicyclo[4.2.0]-2,4,7-octatriene could be excluded. The rearrangements are considered in terms of mechanism. A treatment for forbiddenness-allowedness based on nodal properties is presented and applied to the present chemistry. This is termed MO Following and is a useful new approach in following MO's and drawing correlation diagrams of reacting molecules.

In pursuing the preparation of C_8H_8 hydrocarbons and I their interconversions, $^{1a-i}$ we have thus far described the synthesis of barrelene (1), $^{1a-f}$ semibullvalene (2), 1b and tricyclo[3.3.0.0^{2,6}]octa,3,7-diene (3).^{1h} In this relation, it seemed of interest to study the chemistry of the C_8H_8 carbene, cycloheptatrienylmethylidene (4). It appeared possible that low-energy pathways leading to octavalene (5), cyclooctatetraene, heptafulvene (6), and semibullvalene (2) might exist.



Synthetic Aspects. A reasonable starting point in the desired synthesis seemed to be 7-cycloheptatrienylcarboxamide (7). Lithium aluminum hydride reduction had been reported² to give 7-cycloheptatrienylmethylamine (8), and this was confirmed. Conversion by way of the nitrosourethane (10), as shown in Chart I, afforded cycloheptatrienyldiazomethane (11) which proved to be modestly stable in solution. Its identity was established by its preparation from characterized precursors and by its nmr and ir spectra.

(1) (a) For paper I of the series note: H. E. Zimmerman and R. M. Paufler, J. Amer. Chem. Soc., 82, 1514 (1960); (b) II: H. E. Zimmerman and G. L. Grunewald, *ibid.*, 86, 1434 (1964); (c) III: H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966); (d) IV: H. E. Zim-merman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, merman, R. W. Binkley, R. S. Givens, and M. A. Snerwin, *ibid.*, **89**, 9932 (1967); (e) V: H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968); (f) VI: H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969); (g) VII: H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969); (h) VIII: H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969); (i) IX: H. E. Zimmerman and H. Iwamura, *ibid.*, **92**, 2015 (1970).
(2) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 193 (1960).

(1960).





Results

Rearrangement Studies. The results observed in thermal and photochemical treatment of 11 are summarized in Table I and detailed in the Experimental Section.

In the case of thermal decomposition, the products observed were benzene, cyclooctatetraene, heptafulvene, and acetvlene with the first three products in relative yields of 1:2:2. Product identity was established by comparison of nmr, ir, uv, and vpc retention time with authentic materials. For this comparison heptafulvene was prepared as previously described² and its unreported nmr spectrum was recorded. Because of the complexity of the spectrum it was checked by computer simulation. Spectra of semibullvalene (2), bicyclo[4.2.0]-2,4,7-octatriene (12), and other C₈H₈ isomers were available from previous work in these laboratories.1

Turning to the photochemical results, irradiation of 11 utilized a filter designed to cut off light below 410 nm with the aim of precluding cycloheptatriene absorption and yet allowing the diazo moiety to capture light. From photolysis in cyclopentane at 0°, benzene, COT, and heptafulvene in relative yields of 1:2.4:5.2, respectively, resulted. Absorption by heptafulvene product precluded complete reaction. Low-conversion

Table I. Reaction Product Yields from 7-Cycloheptatrienyldiazomethane

Conditions or reagent	<i>T</i> , °C	Solvent	% SM∘	% Bª	% COT⁴	% Hª	% C₂H₂	% others	% mass balance
Δ	49	C ₅ H ₁₀	0	19	38	37	c		9 4.0 ^b
Δ	95ª	Sat. oil ^e	9.3/	7.6 ¹	3.61	3.61	2.81	$2.0^{g,h}$	27.8
$h\nu > 410 \text{ nm}$	0	$C_{5}H_{10}$	471,1	3.41	8.31	17.6 ^k	с		76.3
$h\nu > 410 \text{ nm}$	-70	$C_{\delta}H_{10}$	85	1.8	5.4	7.6	q		99 .8 ^b
$h\nu$ (sens)	0	C_5H_{10}	12	9,6 ^h	9.5 ^h	$< 1^{m}$	c	$8^{b,h,n}$	27.1
Cu	25 ^d	Sat. oil ^e	0	14.0	18.5	0.22	7.6	2.40.1	35.1 ^b
Cu	- 20ª	$C_{5}H_{10}$	16	13.0	20.7	27.8	9		77.40
Pd(PhCN) ₂ Cl ₂	0	C_5H_{10}	0	35.0	46.7	0	c	<2.4°	84.1 ^b
ZnCl ₂	0	Triglyme	0	22.6	23.0	0	6.3	$10^{f,p}$	55.60

^a SM = starting material, B = benzene, COT = cyclooctatetraene, H = heptafulvene. ^b Yield analyses by nmr. ^c Not trapped. ^d Vola-tile products removed as formed at low pressure. ^e Saturated, purified, paraffin oil. ^f Nmr analysis. ^e Cycloheptatrienyl dimer and/or ether which gave one long retention time vpc peak. ^h Yield analysis by vpc. ^c Ir analysis. ^f Nmr analysis of one solution and vpc of another. ^k Nmr of one solution and uv-visible of another. ^m Uv-visible analysis. ⁿ 4.9% unidentified saturated compound (one vpc peak) plus 3.1% in four minor components (four peaks by vpc). • Nonvolatile material, cycloheptatrienyl by nmr analysis. • Cycloheptatrienyl compound; not 2,3-diazatricyclo[5.3.0.0^{4,10}]deca-2,5,8-triene by nmr analysis. ^a Trapped but obscured by solvent.

photolysis at -70° gave similar results (see Table I). Bicyclo[4.2.0]-2,4,7-octatriene (12) was not detected at this low temperature. Even a 1% yield of this compound would have been detected by nmr analysis judging from the sharp peaks at τ 4.12, 4.37 and 6.68 found in the nmr of authentic 12 and the observed level of sensitivity of detection of the other components. The benzophenone-sensitized photolysis (88% decomposition) in cyclopentane at 0° afforded benzene and COT in equivalent yields and no heptafulvene.

Several catalysts were used and gave relative yields of benzene and COT of about 1:1.3. The formation of heptafulvene (or its stability once formed) was depressed. Acetylene was trapped in several cases.

Interpretative Discussion

The results indicate that there are three competitive processes occurring in the decomposition of cycloheptatrienyldiazomethane (11). These are depicted in Chart II. We note very little difference in products

Chart II. Competitive Pathways in the Reaction of 7-Cycloheptatrienyldiazomethane



obtained by the varying modes of decomposition of 11 (see Table I), and this strongly suggests a common intermediate which is most reasonably taken to be cycloheptatrienylmethylidene (4).

The reaction to form benzene and acetylene is most rationally envisaged as deriving from the norcaradiene valence tautomer 13; note eq 1. Comparison of the nmr of cycloheptatrienyldiazomethane (11) and its precursors with spectra described for known cycloheptatriene and known norcaradiene species³⁻⁷ (note Table II) shows the C-1 hydrogens of 11 to be typically

(3) J. A, Berson and M. R. Willcott, III, J. Amer. Chem. Soc., 88, 2494 (1966).

vinylic for the several derivatives presently studied. Nevertheless, ca. 8% norcaradiene could conceivably be present. This means that the valence tautomerism to give the norcaradiene isomer 13 must occur once carbene 4 has been generated.⁸ A less likely rationale accounting for the considerable amount of product derived from 13 is that the minor amount of norcaradiene valence tautomer of the diazo compound 11 present in equilibrium reacts at a rapid rate relative to the cycloheptatrienyl tautomer, thus compensating for its lower concentration.

Fragmentation reactions of cyclopropyl carbenes are well known.⁹ This general process can be pictured as a cheletropic¹⁰ reaction.

The second reaction observed is the formation of heptafulvene from the reaction of cycloheptatrienyldiazomethane (11). This transformation involves the well-known 1,2-hydrogen migration of carbenes to give alkenes. Thus, the literature of carbenes reveals that whenever there is a C-H bond adjacent to the valencedeficient center, a particularly facile rearrangement occurs to generate a π system.¹¹ Thus heptafulvene formation can be envisaged as



Finally, the third transformation found is the formation of cyclooctatetraene. A priori, three mecha-

(8) However, acetylene expulsion can occur subsequent to six-ring closure or concerted with it.

⁽⁴⁾ E. Ciganek, ibid., 89, 1454 (1967).

⁽⁷⁾ E. Ciganes, *ibid.*, **89**, 1494 (1907).
(5) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *ibid.*, **78**, 5448 (1956).
(6) E. Ciganek, *ibid.*, **88**, 741 (1966).
(7) E. Ciganek, *ibid.*, **87**, 1159 (1965).

⁽⁹⁾ L. Friedman and H. Shechter, J. Amer. Chem. Soc., 82, 1002 (1960); S. J. Cristol and J. K. Harrington, J. Org. Chem., 28, 1413 (1963); P. K. Freeman and D. G. Kuper, ibid., 30, 1047 (1965); R. G. Bergman and V. J. Rajadhyadsha, J. Amer. Chem. Soc., 92, 2164 (1970); M. Jones, Jr., S. D. Reich, and L. T. Scott, *ibid.*, 92, 3118 (1970)

⁽¹⁰⁾ R. B. Woodward and R. Hoffmann, "The Conservation of rbital Symmetry," Verlag Chemie, Academic Press, Weinheim/ (10) K. B. TOLE Orbital Symmetry," Verlag Chemie, Gergstr., Germany, 1970, Chapter 10. (11) W. Kirmse, "Carbene, Carbenoide und Carbenanaloge,"



Substituents ^a	Pre- ferred	N			
$\mathbf{R}_{7a}, \mathbf{R}_{7b}, $ other	form	H_1 and H_6	H_2 and H_5	H_3 and H_4	Ref
$\mathbf{R}_{7a} = \mathbf{R}_{7b} = \mathbf{R}_1 = \mathbf{C}\mathbf{H}_3$	A	4.8-5.2	4.3-3.6		е
$R_{7a} = R_{7b} = R_2 = CH_3$	Α	4.8-5.2	3.8-4.2	3.6-3.8	е
$R_{7a} = R_{7b} = R_3 = CH_3$	Α	4.8-5.1	3.9-4.2	3.7-3.9	е
$R_{7a} = CM$	Α	4.91	3.93	3.53	f
$R_{7a} = CO_2Et$	Α	4.63	3.86	3.44	This work, g
$R_{7a} = CONH_2$	Α	4.62	3.6-3.2		This work
$\mathbf{R}_{7a} = \mathbf{C}\mathbf{H}_2\mathbf{N}\mathbf{H}_2$	Α	4.82	3.90	3.47	This work
$R_{7a} = CH_2 NHCO_2 Et$	Α	4.80	3.90	3.46	This work
$R_{7a} = CH_2N(NO)CO_2Et$	Α	4.96	3.90	3.42	This work
$\mathbf{R}_{7a} = \mathbf{C}\mathbf{H}_{2}\mathbf{N}(\mathbf{C}\mathbf{H}_{3})_{3}\mathbf{I}$	Α	4.95	3.90	3,50	This work
$R_{7a} = CHN_2$	\mathbf{A}^{b}	4.86	3.88	3.41	This work
$\mathbf{R}_{7a} = \mathbf{R}_{7b} = \mathbf{C}\mathbf{N}$	В	6.53	3.72	3.48	h
$R_{7a} = R_{7b} = CN; R_1 = R_4 = CH_3$	В	6.88	Centered at 3.8		f
$R_{7a} = R_{7b} = CN; R_2 = R_5 = CH_3$	В	6.78		3.81	f
	$(A + B)^{c}$	5.3	3.8-3.2		i
	Ad	4.6	3.8-3.2		i
$R_{7a} = CN; R_{7b} = CF_3$	Bª	7.05	3.8	-3.2	<i>i</i>

^a Unspecified R = H. ^b Spectrum unchanged from +20 to -70° . ^c Average spectrum above -85° , approximately 80% A. ^d At -114°. Reference 3. Reference 4. Reference 5. Reference 6. Reference 7.

nisms seem reasonable. The first (note eq 3a) is the ring expansion of the norcaradiene valence tautomer 13 to give bicyclo[4.2.0]-2,4,7-octatriene (12) which is known to be unstable relative to cyclooctatetraene. Such ring expansion has precedent in the formation of cyclobutene from cyclopropylmethylene.¹² However, in the photochemical runs at -70° this bicyclic intermediate (i.e., 12) would have been observed (note Experimental Section). It has been reported¹³ to be stable at -30° and this has been confirmed in our laboratories in connection with other studies.^{li} Furthermore, in our earlier studies we have shown^{li} that bicyclo[4.2.0]-2,4,7-octatriene (12) gives rise to benzene and not cyclooctatetraene on photolysis; thus the presence of COT cannot be ascribed to subsequent photolysis of 12.

The second mechanistic pathway for formation of cyclooctatetraene is a direct ring expansion of carbene 4. The literature suggests that both alkyl groups and π moieties β to a carbenoid center migrate readily, although there is relatively little quantative information on this point.¹⁴ This reaction is pictured in eq 3b.

The third mechanistic possibility involves an addition of the carbone carbon to an adjacent double bond to give octavalene 5 which then opens to cyclooctatetraene (eq 3c). This mechanism requires that the octavalene be unstable at -70° . Of the three mechanisms, that in eq 3b seems preferable in view of the nonobservation of the potential intermediates 12 and 5.

MO Following. A New Approach to Drawing Correlation Diagrams and Following Reactions. Having

(15) L. Hellerman and R, L, Garner, J. Amer. Chem. Soc., 57, 139 (1935); H. E. Zimmerman and J. H. Munch, ibid., 90, 187 (1968).



now considered the gross features of the three reactions encountered, we now find it of interest to consider electronic details of the reactions observed.

In analyzing the present reactions, we find that the usual methods do not generally apply. For only one of the reactions is there any symmetry to allow construction of a correlation diagram. The Hückel-Möbius methods¹⁶ presented by us earlier require a cyclic array of orbitals; however, the present reactions consist (vide infra) of linear arrays of orbitals instead.

As a consequence, an approach allowing treatment of reactions where the molecule consists of a linear array of orbitals as it proceeds from reactant to product was developed. Four basic rules are utilized in this approach: (1) the number of nodes in a MO does not change during reaction;^{17a} (2) as is well known, the

⁽¹²⁾ W. Kirmse and K. H. Pook, Chem. Ber., 98, 4022 (1965).
(13) E. Vogel, H. Kiefer, and W. R. Roth, Angew. Chem., Int. Ed. Engl., 3, 442 (1964).

⁽¹⁴⁾ That alkyl groups can migrate is seen in the ring expansion of cyclopropylcarbene as cited above and the ring contraction of cyclobutylidene. The facile π migration is seen in the rearrangement of 2,2,2-triarylethylidene.15

⁽¹⁶⁾ H. E. Zimmerman, *ibid.*, 88, 1564 (1966). (17) (a) It should be noted that this is true only for acyclic systems, and for totally cyclic systems. For cyclic systems with side chains the total number of nodes sometimes does change. (b) This is true only for linear systems unless further constraints are put on the rule. This represents a tendency of actual systems to conform to the exact symmetry observed for systems composed only of p orbitals. Furthermore, just as the noncrossing rule based on geometric symmetry is not absolute for systems beyond diatomics, the present rule will also have



Figure 1. Cheletropic disengagement of acetylene from ethylene with cyclopropylmethylene as reactant: i, degenerate at geometry of **14a**; j, degenerate at geometry of **14c**; k, numbers in parentheses are the nodal possibilities as a consequence of using only rule 3. The sequences, +1 + 2 + 3 - 4 - 5 - 6, signify only the signs weighting the basis set orbitals in the MO's; quantitative weightings are not implied and nodes may be shifted somewhat.

number of nodes of a linear system increases with increasing MO energy; (3) the array of nodes in any given MO of a linear system is approximately symmetrically disposed in pairs, with respect to the center of the array; (4) MO's consisting of the same parity (*i.e.* evenness or oddness of number) of nodes will tend not to cross.^{17b} The application of these rules is demonstrated by dealing with the reactions at hand. In the one case where symmetry is available as a tool for construction of the correlation diagram, both the symmetry and nodal property methods are used and are seen to be in agreement.^{17c}

Turning first to the benzene-acetylene formation, we note that the reaction is the microscopic reverse of the addition of one end of an acetylene molecule across a two-center π system. This is depicted in Figure 1. The carbene decomposition is thence a fission to afford two orthogonal acetylenic π systems plus the two-center π moiety which presently is benzenoid but for simplicity can be pictured as ethylenic. Formation of three such π systems from two strained cyclopropane σ bonds is certain to be highly exothermic, especially where one of the π systems is benzenoid.

Interestingly, one can deduce a preference for one geometry of the carbene during rearrangement. Figure 1 reveals that in the products 14c there are two bonding π systems which are symmetric with respect to the vertical plane (σ) and one bonding antisymmetric π system. These are labeled π_{34} , $\pi_{12} + \pi_{56}$, and $\pi_{12} - \pi_{56}$ π_{56} , respectively. The latter two are exactly equivalent to vertically and horizontally oriented π orbitals. In the reactant (14a in Figure 1) the σ bonds form a symmetric combination, $\sigma_{23} + \sigma_{45}$, and an antisymmetric combination $\sigma_{23} - \sigma_{45}$. Additionally, at the exocyclic carbon atom there is a horizontal p orbital which is $p_h = p_1 - p_6$ and also a vertical p orbital, namely $p_v = p_1 + p_6$. The former is antisymmetric with respect to the vertical plane and the latter is symmetric. Recognizing that whichever orbital is selected to accept the carbene electron pair will also have added s character, we see that depending on which terminal p orbital, $p_1 + p_6$ (vertical) or $p_1 - p_6$ (horizontal), is utilized for the electron pair, there will be different carbon-hydrogen orientation. However, only $p_1 + p_6$ is symmetric with respect to the plane σ and can correlate with the bonding product orbital which is symmetric. Because

exceptions. (c) It should be noted that these rules are based on idealized systems lacking differential electronegativity and represent a tendency of the molecule to conform to the same wave-function behavior.



Figure 2. Rearrangement of carbenes with hydrogen migration to give ethylenes: i, degenerate at the geometry of 16a; k, numbers in parentheses are the nodal possibilities as a consequence of using only rule 3. The sequences, +1 + 2 + 3 - 4 - 5 - 6, signify only the signs weighting the basis set orbitals in MO's; quantitative weightings are not implied and nodes may be shifted somewhat.

 $p_1 + p_6$ is vertical the electron pair of the carbene must become oriented in an sp² hybrid which is in the vertical plane and similarly the C-H bond must become so oriented. Any tendency to orient horizontally is avoided since then a bonding reactant MO will correlate with an antibonding one (see the correlation diagram in Figure 1) to give a forbidden reaction.

This prediction of vertical orientation, in a plane bisecting the three ring, is consonant with the observed cheletropic fissions of the type having restricted geometry. The case of tricyclo[$2.2.1.0^{2.6}$]-3-heptylidene (15) is one example¹⁸ where such geometry is provided in a rigid reactant molecule and where the reaction proceeds in uniquely facile manner. Note eq 4.



The same correlation is possible without the explicit use of symmetry utilizing the nodal correlations men-

(18) (a) S. J. Cristol and J. K. Harrington, J. Org. Chem., 28, 1413 (1963); (b) see also the case of tetracyclo[3.2.1.0^{2.7}.0^{4.6}]-3-octylidene described by R. G. Bergman and V. J. Rajadhyaksha, J. Amer. Chem. Soc., 92, 2164 (1970).

tioned above. The approach, while very closely related in the present instance to symmetry usage, has the advantage of being applicable to systems without symmetry.

Rule 3 above allows assignment of some of the unknown nodes of the reacting species just prior to and after reaching transition-state species 14b. The MO's are analogous to those in hexatriene which is isoelectronic. Now, in both reactant and product, one can determine the number of nodes present in each MO. Initial inspection of these species reveals only MO's localized at some of the atoms of the six present. It is necessary to recognize that an infinitesimal perturbation of these structures toward transition state will bring in weighting of all six orbitals and that the weightings and signs of orbitals will approach those found for the transition-state species 14b. Thus, in determining nodes for the reactant 14a and product 14c, we will include all orbitals. Each of the reactant and product MO's now may be assigned a nodal structure by use of the four rules. For example, in 14c for MO π_{34} there is no central node by virtue of the bonding nature of this orbital. Rule 3 tells us that the remaining orbitals and thence nodal possibilities will be symmetrically displayed with respect to the center of the array. If all remaining orbitals are positively weighted, then there will be 0 nodes in π_{34} . Each half of the orbital array can alternatively have 1 or 2 nodes leaving the possibilities of 0, 2, or 4 nodes totally for the MO.

Similarly in 14c, MO π_{12} - π_{56} must have an odd number of nodes since all others must occur in pairs (*i.e.*

rule 3). There may be nodes at both 2–3 and 4–5 or at neither, this being required by the need for symmetrical disposition of nodes. This leads to 1 or 3 as the total nodes potentially possible for this MO. Assignment of possible nodes is made to the rest of the MO's in Figure 1 by the same method. Of the number of nodes considered tentatively in each case, one is selected by correlation with the number of nodes in the transition state species 14b. Here we make use of the noncrossing rule (rule 4) and the increasing number of nodes with energy. The correlation diagram is completed by drawing in all correlation lines using the noncrossing rule. The agreement with the correlation obtained using molecular symmetry in this case is not fortuitous but does add confidence to the method.

Turning now to the rearrangement of cycloheptatrienylmethylene (4) to give heptafulvene (6), it is of interest to consider generally the rearrangement of carbenes with 1,2-hydrogen migration to give olefins. The gross orbital changes are given in Figure 2 together with an energy level diagram. Again, resort is made to the linear orbital array at the reaction midpoint. Thus, when partially rearranged, the molecule will have a linear array of four orbitals as in 16b. This linear array is "butadiene-like" and the MO's will be ordered as shown beneath this species. The number of nodes in each MO is given in parentheses and the signs weighting the basis set orbitals are given schematically; thus MO 1 is designated +1 + 2 + 3 + 4 and MO 2 as +1 + 2-3 - 4, etc. With changing electronegativities and overlaps, the positions of the nodes may shift but should not change in number. For the reactant and product as in the previous example, the number of nodes is less obvious at the outset. Thus, in reactant 16a, the lowest energy MO is σ_{23} which has no internal nodes. But this MO includes infinitesimal weightings of AO's 1 and 4. A basic assumption (rule 3) throughout is that the "symmetry" established by the known portion in a given MO will be the same as in the unknown portion. Thus here, since σ_{23} is symmetric, the orbital 1 must have the same sign as 4. If these signs are the same as 2 and 3, there will be no nodes in MO 1; and if they are different, there will be two nodes (*i.e.* between orbitals 1 and 2 as well as between 3 and 4). The same type of reasoning allows assignment of nodes for other MO's. An additional assumption (rule 4) permits further definition of the number of nodes, and this is noncrossing of MO's of the same parity of nodes (e.g., two MO's with an even number of nodes will not cross) together with the knowledge (rule 2) that energy increases with increasing number of nodes. MO's with the same number of nodes then correlate.

Inspection of Figure 2 shows an interesting effect on the reactant. It is seen that the p orbital combination correlating with bonding transition state and product MO's is $p_1 - p_4$; this is the MO which has added s character to be approximately sp^2 hybridized and which is doubly occupied. We note that this is oriented horizontally in back of the drawing, signifying that the right hydrogen must bend forward horizontally in the reactant for rearrangement. This is what is seen to be needed geometrically to end up with a stable alkene system. Hydrogen bending vertically would require the electron pair to be in an orbital which was $s + (p_1 + p_4)$ weighted and we note that $p_1 + p_4$ correlates with an antibonding MO and this would represent a forbidden process.

A final comment is needed regarding the basis of the nodal treatment of correlation diagrams. The method assumes¹⁹ that in an array of orbitals the array of nodes will be relatively regular with respect to the center of the orbital array. Differences in electronegativities and overlaps may displace nodes and change their relative location to some extent but should not change the basic pattern of nodes.^{19a}

Experimental Section

Reagents and Solvents. Removal of unsaturated impurities from 21. of paraffin oil (American Oil Co., No. 31 USP) was accomplished by washing with fuming sulfuric acid and with 10% sodium hydroxide, and filtration through Celite and sodium sulfate, followed by heating to 170° at 0.04 mm for several hours. Cyclopentane (1 1.) was purified by washing (six 50-ml portions) with fuming sulfuric acid followed by water washing, drying (MgSO₄), and slow distillation through a 115 \times 2 cm stainless steel helipak column. A small amount of lower boiling saturated impurity remained which did not interfere with vpc, nmr, or uv-visible measurements. Cyclohexane for chromatography purposes was redistilled from commercially available cyclohexane. Benzophenone for sensitization was recrystallized five times from ethanol. Bis(benzonitrile)palladium dichloride was prepared by the method of Kharasch, *et al.*²⁰

Analytical Methods and Equipment. Vapor-phase chromatography was carried out on two columns, A and B. A was a 24 ft \times ¹/₄ in. analytical column packed with 15% Carbowax on 60-80 mesh Chromosorb W, and B was an 18 ft \times ³/₈ in. preparative column packed with 15% Carbowax on 60-80 mesh Chromosorb W. The molar response of the flame ionization detector was calibrated with standard mixtures of benzene, *p*-xylene, cyclooctatetraene, and mesitylene. The procedure for nmr analysis was to add 0.100 ml of 0.001 *M* standard *p*-dibromobenzene in cyclopentane or carbon tetrachloride to 0.40 \pm 0.005 ml of the solution to be analyzed. An average of at least five integral traces was used in calculations. The relative error in reported yields was less than 10%. Elemental analyses were performed by Galbraith Laboratories, Inc. Melting points were taken on a hot-stage apparatus and are corrected.

Filter Solutions. Filters A and B were used for direct and sensitized photolyses, respectively: filter A, ferric chloride (0.075 *M*) in 0.10 *M* hydrochloric acid; transmission (above 410 nm) 250-403 nm, 0.0%; 409 nm 0.1,%; 425 nm, 10.0%; 443 nm, 50%; 483-700 nm, 90%; filter B, copper sulfate pentahydrate 12.0 g/l., nickel sulfate hexahydrate 154.0 g/l., cobalt sulfate heptahydrate 344.0 g/l., and potassium nitrate 8.0 g/l. in aqueous solution; transmission (275-373 nm, maximum at 330 nm) 200-275 nm, 0.0%; 293 nm, 5.0%; 302 nm, 10.0%; 330 nm, 63.0%; 357 nm, 10.0%; 360 nm, 5.0%; 373-405 nm, 0.0%; 419 nm, 0.75%; 435-532 nm, 0.0%.

Ethyl 7-Cycloheptatrienylcarboxylate. Using a method analogous to those described by Doering, Linstrumelle,²¹ and others, 20.0 g (0.176 mol) of ethyl diazoacetate was added in two equal portions to 21. of benzene and photolyzed through Pyrex after each addition with a 450-W medium-pressure Hanovia uv lamp. Two photolysates were combined, concentrated *in vacuo*, and steam distilled at reduced pressure with the boiling point adjusted to 55–65°;

⁽¹⁹⁾ It is important to clarify that rule 1 is predicted on a reaction in which there is no switching of lobes on a given atom overlapping with an adjacent orbital. For example, in the 180° twisting of ethylene, bonding MO 1 develops one new node as it becomes antibonding; this is due to such lobe switching, For such reactions one would need to subtract nodes developed by lobe switching.

⁽¹⁹a) NOTE ADDED IN PROOF. MO Following turns out to be more general and operates with minor modification for nonlinear systems. Rule 4 becomes modified to add "MO's tend not to cross if their local nodal character matches at the onset of bonding." Using "half-reaction MO's" one can readily derive correlation diagrams for signatropic rearrangements, 1,2-alkyl shifts, 1,2-vinyl migrations, 1,2-aryl rearrangements, carbene insertions, and carbene additions, as well as many more reactions not susceptible to known treatments.

⁽²⁰⁾ M. S. Kharasch, R. C. Seyler, and F. R. Mayo, J. Amer. Chem. Soc., 60, 882 (1938).

⁽²¹⁾ G. Linstrumelle, Tetrahedron Lett., 85 (1970).

the distillate was ether extracted and the organic phase was dried (Mg SO₄) and concentrated in vacuo to give 23.578 g of clear yellow oil containing 83% desired isomer by nmr analysis²² (34% yield). Although this oil was used without further purification, distillation gave a clear colorless liquid of greater purity, bp 87° (4.0 mm) (lit. 20 86° (6 mm)).

7-Cycloheptatrienylcarboxamide. Ethyl 7-cycloheptatrienylcarboxylate (20.448 g, 0.015 mol due to 84% purity) and 80 ml of concentrated ammonium hydroxide were stirred in the dark under nitrogen at room temperature for 4 days. Refrigeration for 2 days followed by suction filtration and washing with 30 ml of cold pentane left 9.16 g of yellow crude product. This material was digested briefly in 300 ml of warm ethyl ether and filtered to give 5.542 g of white platelets, mp 145-146° (lit.20 145-146°). Repeated concentration of the filtrate gave an additional 2.170 g of amide, mp 137-142° (total yield 54%).

The pure amide was stable under vacuum for several months in the freezer; however, the melting point dropped to 137-143° after several hours in the atmosphere. The average yield for many preparations was 47 %.

7-Cycloheptatrienylmethylamine. The lithium aluminum hydride method of Doering and Wiley² was carried out on 8.055 g (0.0598 mol) of 7-cycloheptatrienylcarboxamide to give after distillation 4.056 g (0.0335 mol, 56%) of clear colorless liquid, bp 67.0° (4.65 mm) (lit.² 56.5° (4.2 mm)).

Ethyl N-(7-Cycloheptatrienylmethyl)carbamate. A 20-ml solution of 5.35 g (0.0493 mol) of ethyl chloroformate in absolute ethanol was added dropwise to 30 ml of absolute ethanol containing 5.957 g (0.0491 mol) of 7-cycloheptatrienylmethylamine and 5.58 g (0.055 mol) of triethylamine. After a 2-hr reflux period the solvent was removed at reduced pressure and the residue washed repeatedly with ethyl ether. The ether washings were filtered, dried (Na_2SO_4) , and concentrated in vacuo to leave 8.991 g (95%) of clear, viscous liquid. The spectral data were: ir (CCl_4) 2.9 and 2.98 (NH), 3.31–3.5 (CH), 5.81 (C=O), 6.62 and 8.17 μ ; nmr (CCl_4) τ 3.46 (t, 2 H, J = 3 Hz, 7-cycloheptatrienyl 2,5 protons), 4.22 (m, 1 H, NH), 4.80 (d of d, 2 H, J = 9.0 Hz split by 5.5 Hz, 7-cycloheptatrienyl 1,6 protons), 5.95 (q, 2 H, J = 8 Hz, $-OCH_2CH_3$), 6.59 (t, $2 H, J = 8 Hz, -CH_2NH-$, 7.8-8.3 (broad quintet, 1 H, J = 8 Hz, 7-cycloheptatrienyl 7 proton), 8.83 (t, 3 H, J = 8 Hz, $-OCH_2CH_3$).

This material which was pure by nmr analysis was used without further treatment. An analytical sample was gradient (25-70°) distilled at 0.015 mm.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.23. Found: C, 68.15, H, 7.91; N, 7.09.

EthylN- Nitroso-N-(7-cycloheptatrienylmethyl)carbamate. Using the general procedure of White,²³ a solution of 2.00 g (10.3 mmol) of ethyl N-(7-cycloheptatrienylmethyl)carbamate in 15 ml of carbon tetrachloride was added to an ice-cooled yellow slurry formed by stirring 2.46 g (30.0 mmol) of powdered sodium acetate and 11.0 mmol of dinitrogen tetroxide in 50 ml of carbon tetrachloride for 30 min. The dinitrogen tetroxide was delivered as a 0.45 Mcarbon tetrachloride solution standardized by thiosulfate titration of N_2O_4 -oxidized iodide. After the 0° addition the resulting orange slurry was stirred for 20 min and washed (five 100-ml portions) with 5% aqueous sodium carbonate, and the organic phase was dried (MgSO₄) and concentrated at reduced pressure with the temperature held below 30°. The resulting 2.27 g of oil (13% starting material by nmr analysis²⁴) was purified by liquidliquid chromatography at 28.5°. A 150×4.5 cm column was dry packed with 798 g of Celite (Eagle-Picher Co., Celaton FW-80) bearing 531 g of the lower phase from a cyclohexane (1000 ml), dimethylformamide (400 ml), ethyl acetate (250 ml), and water (30 ml) mixture. Elution with the upper phase of this solvent system and collection of 20-ml fractions which were worked up by water extraction, drying, and concentration in vacuo gave: fractions 1-70, nil; 71-82, 0.152 g of a mixture containing starting material, some desired product, and overnitrosated compound; 83-90, 1.212 g (57%) of pure product; 90-95, 0.115 g of desired product contaminated by an aromatic substance. The product from fractions 83-90 had the following spectral data: ir (CCl₄) 3.3-3.5(CH), 5.72 (C=O), 6.60, 7.01, 7.12, 7.23 (N-N=O), and 8.75 μ ; nmr (CCl₄) τ 3.42 (t, 3 H, J = 3 Hz, 7-cycloheptatrienyl 3,4 protons), 3.90 (d of m, 2 H, J = 9 Hz, 7-cycloheptatrienyl 2,5 protons), 4.96 (d of d, 2 H, J = 9 Hz split by 6 Hz, 7-cyclohep-

(24) R. A. Moss, Tetrahedron Lett., 711 (1966).

tatrienyl 1,6 protons), 5.52 (q, 2 H, J = 7 Hz, ---CH₂CH₃), 6.02 (d, 2 H, J = 7.5 Hz, --CH₂N), 8.03 (broad quintet, 1 H, J = 7.5Hz, 7-cycloheptatrienyl 7 proton), 8.58 (t, 3 H, J = 7 Hz, $-CH_2CH_3$).

The pure N-nitrosocarbamate was stable under vacuum for several weeks in the freezer; however, after longer periods or at higher temperatures decomposition was evident and repurification was necessary.

7-Cycloheptatrienyldiazomethane. A 15-ml cyclopentane solution containing 0.83 g (3.72 mmol) of ethyl N-nitroso-N-(7-cycloheptatrienylmethyl)carbamate was added dropwise to a stirred 0° slurry composed of 5.0 ml of 3 M methanolic sodium methoxide and 15.0 ml of cyclopentane. After 1.25 hr of stirring in the dark under nitrogen the slurry was washed (four 40-ml portions) with 0° 5% aqueous sodium hydroxide and the organic phase was dried for 3 min over sodium hydoxide pellets. Filtration gave 32.0 ml of clear yellow solution with the following spectral data: uv-visible λ_{max} (cyclopentane) 224 (ϵ 11,600), 250 shoulder (ϵ 5300), 300 tail (\$ 850), 380-450 (\$ 13), and 500-nm tail (\$ 3.6); ir (cyclopentane) 4.85 (very strong, CH=N₂) 6.3, 7.2, 9.2, 13.5, and 14.4 μ ; ir (CCl_4) 3.3, 3.4, 3.5, 4.85 $(C=N_2)$, 6.25, 7.15, and 14.3 μ ; nmr (cyclopentane) τ 3.41 (t, 2 H, J = 3 Hz, 7-cycloheptatrienyl 3,4 protons), 3.88 (d of m, 2 H, J = 9 Hz, 7-cycloheptatrienyl 2,5 protons), 4.86 (d of d, 2 H, J = 9 Hz split by 5.5 Hz, 7-cycloheptatrienyl 1,6 protons), 6.26 (d, 1 H, J = 5.5 Hz, $-CH = N_2$). Solvent side bands occurred above τ 7.3 and obscured the quartet expected at τ 7.48 which was observed in a carbon tetrachloride solution.

The yield was measured to be 2.94 mmol (79%) by nmr analysis with *p*-dibromobenzene internal standard. Decomposition of 0.50 ml of the diazo solution liberated 1.10 ml of nitrogen indicating 2.83 mmol (76%) of the desired product. The nmr measurement was found to be more reproducible and generally 5% lower than the nitrogen evolution method.

Trimethyl-7-cycloheptatrienylmethylammonium Iodide. The method of Doering and Wiley² was utilized to transform 1.00 g (8.3 mmol) of 7-cycloheptatrienylmethylamine into 1.623 g (67.5%) of trimethyl-7-cycloheptatrienylmethylammonium iodide, mp 194.5 -195.5° (lit.² 194-195°).

Heptafulvene. A low-pressure room temperature Hofmann elimination was carried out as described by Doering and Wiley² on the trimethyl-7-cycloheptatrienylmethylammonium hydroxde derived from the iodide. The heptafulvene collected at 77°K gave the following spectra data: nmr (-44°, CDCl₃) τ 3.93 (s or a 1-Hz d, 0.66 H), 4.13 (narrow m, 1.37 H, 1.5-Hz coupling), 4.42 (m, 3.18 H, 1.5- and 3-Hz splitting), 4.68 (three-peak m, 0.88 H, separated by 5 and 6 Hz), 5.54 (s, 2.0 H, $=CH_2$); uv-visible λ_{max} (cyclopentane) 223 shoulder (ϵ 60,700), 321 min (ϵ 14,500), 243 (e 15,080), 252 (e 13,770), 265 (e 12,600), 278 (e 13,680), 283 (e, 12,940), 293 shoulder (¢ 10,640), 344 min (¢ 347), 369 (¢ 446), 392 (¢ 521), 414 (¢ 522), 448 (¢ 411), 485 (¢ 242), 527 (¢ 108.6), and 573 nm (ϵ 38.1). The nmr spectrum also had small peaks at τ 2.60, 5.33, 6.70, and 8.8 (total integral 1.28 H) due to impurities. The expected trimethylamine absorption at τ 7.8 (s, 8.1 H) was observed. The maxima in the uv coincided with those reported by Doering and Wiley;² however, our reported maxima in the visible were slightly (<10 nm) blue shifted as λ increased.

Verification of the heptafulvene structure and the assignment of nmr chemical shifts were achieved by computer simulation²⁵ of the 60- and 100-MHz spectra. Excellent agreement was obtained with the use of coupling constants reported by Bertelli, et al., 26 for 8,8dicyanoheptafulvene when the chemical shifts were assigned as τ 4.05, 4.42, and 4.58 for ring protons 1,6, 3,4, and 2,5, respectively.

In the presence of air, haptafulvene formed a complex mixture of cycloheptatrienyl ethers, alcohols, and other oxidation products plus the polymer previously reported.²⁰

Reaction of 7-Cycloheptatrienyldiazomethane at 49°. A 22.75-ml cyclopentane solution containing 2.06 mmol (nitrogen evolution and nmr analyses) of 7-cycloheptatrienyldiazomethane was refluxed for 1.5 hr. The resulting red solution had no $4.85 - \mu$ diazo peak and the nmr spectral data were: nmr (cyclopentane) (relative integrals given as the second item in parentheses) τ 2.78 (s, 1.0, benzene), 4.33 (s, 2.9, cyclooctatetraene), 4.55 (m, 0.79, heptafulvene), 5.63 (s, 0.65, heptafulvene = CH_2), spectrum obscured by solvent above τ 7.1. The use of p-dibromobenzene internal stan-

⁽²²⁾ J. A. Berson, D, R. Hartter, H. Klinger, and P. W. Grubb, J. Org. Chem., 33, 1669 (1968). (23) E. H. White, J. Amer. Chem. Soc., 79, 5832 (1957).

⁽²⁵⁾ D. F. Juers, R. J. Boettcher, V. J. Hull, and H. E. Zimmerman, "NMR" Simulator (DECUS-8-194), Digital Equipment Computer Users Society, Maynard, Mass.

⁽²⁶⁾ D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, J. Amer. Chem. Soc., 91, 5286 (1969).

dard allowed the determination of 0.39 mmol (19%) of benzene, 0.79 mmol (38%) of cyclooctatetraene, and 0.76 mmol (37%) of heptafulvene and a 94% mass balance.

The solution was bulb-to-bulb distilled (0.5 mm) to give 0.123 g of clear, yellow oil and 22 ml of light yellow distillate which was shown by vpc at 80° on column A to contain only benzene and cyclooctatetraene. The residue was shown by nmr and ir both before and after liquid-liquid chromatography to be a mixture of oxidized cycloheptatrienyl compounds. No 2,3-diazatricyclo-[5.3.0.0^{4, 10}]deca-2,5,8-triene was detected.

Thermal Reaction of 7-Cycloheptatrienyldiazomethane at Reduced Pressure. A 14.8 ml cyclopentane solution containing 2.8 mmol (nitrogen evolution and nmr analyses) of 7-cycloheptatrienyldiazomethane was added to 30.0 ml of stirred, purified paraffin oil (American Oil Co., No. 31 USP) at 0°. Cyclopentane (pure by nmr analysis) was removed at 0° (0.6 mm) and 0.40 ml of deuteriochloroform was placed in a receiver and cooled to 77°K. The evacuated (1.1–1.5 mm) system was heated; at 95° rapid evolution of gas began and a red oil was collected in the 77°K receiver. After 30 min at 95°, bubbling subsided and a temperature increase to 195° caused no further visible product collection.

The product was a mixture of red solids at 77°K but became a vigorously bubbling deuteriochloroform solution at -78° with the following nmr spectrum: nmr $(-30^{\circ}, \text{CDCl}_3, \text{ relative in$ tegrals given as the second item in parentheses) τ 2.75 (s, 4.44, benzene), 3.30 (t, 1.82, J = 3 Hz, diazo reactant), 3.5 (m, 0.25), 3.68-4.0 (d of m, 1.89, J = 9 Hz split by 1.5 Hz, diazo reactant), 4.05 (m, 0.35, heptafulvene), 4.15 (m shoulder on cyclooctatetraene s, 0.53, heptafulvene), 4.31 (s, 5.1, cyclooctatetraene), 4.50 (m, 1.1, 1.5-Hz splitting evident, heptafulvene), 4.83 (d of d, 2.1, J =9 Hz split by 5.5 Hz, diazo reactant), 5.60 (s, 0.70, heptafulvene ==CH₂), 6.31 (d, 0.9 J = 5.8 Hz, diazo reactant), 6.38 (d, 0.11, J = 7 Hz, the downfield peak is obscured by the τ 6.3 d), 6.65-6.82 (m of four sharp peaks, 1.3, unidentified), 7.1-7.4 (broad m, 0.6, unidentified), 7.6 (broad q, 1.0, J = 5.5 Hz with smaller splitting, diazo reactant), 8.26 (s, 0.55, probably acetylene), 8.5 (s, 20, cyclopentane), 9.1 (s, 0.8, cyclopentane impurity). The τ 8.26 singlet disappeared when the sample was warmed to room temperature and the 7-cycloheptatrienyldiazomethane peaks decreased in intensity relative to the other peaks. The uv-visible had shoulders at 575, 527, 483, 450, and 413 nm and the general features expected for heptafulvene superimposed on a spectrum of benzene and cyclooctatetraene. Nmr analysis before warming gave: benzene (0.213 mmol, 7.6%), cyclooctatetraene (0.148 mmol, 5.3%), heptafulvene (0.102 mmol, 3.6%), unreacted 7cycloheptatrienyldiazomethane (0.261 mmol, 9.3%), acetylene (0.080 mmol, 2.8%), and the substance(s) responsible for the τ 6.38 d and the 6.65-6.82 m (2.0% by vpc (vide infra)); recovery, 27.8%.

After similar thermal decomposition of the residual 7-cycloheptatrienyldiazomethane three products were collected by preparative vpc at 80° on column B. The first two peaks proved to be (vpc retention times and subsequent nmr spectra) benzene and cyclooctatetraene, respectively. A later $(3.2 \times \text{cyclooctatraene})$ retention time) and smaller peak gave an oil with ir and nmr spectra which suggested the presence of a cycloheptatrienyl ether. The τ 6.38 and 6.65-6.82 peaks accounted for 46% of the oil's nmr spectrum. The yield of this compound was estimated by analytical vpc on column A at 80° to be \simeq 5.6 mg (1.9%) by weight). **Direct Photolysis of 7-Cycloheptatrienyldiazomethane at 0°**. A

Direct Photolysis of 7-Cycloheptatrienyldiazomethane at 0° . A 550-ml cyclopentane solution at 0° containing 6.0 mmol (nmr analysis) of 7-cycloheptatrienyldiazomethane was purged with nitrogen for 20 hr (4.85- μ diazo peak undiminished) and irradiated through filter A (transmission above 410 nm) using a 450-W Hanovia medium-pressure uv lamp housed in a quartz immersion well. The formation of a red internal filter essentially stopped the photolysis of 7-cycloheptatrienyldiazomethane after 3 hr with 57% (ir 4.85- μ analysis) of the compound unreacted. The postphotolysis uv-visible spectrum demonstrated that heptafulvene was absorbing nearly 86% of the incident light above 410 nm.

The reaction solution was distilled at reduced pressure to give 29.1 ml of residue which had not been heated above 10° and which gave the following spectra: ir (cyclopentane) 4.85, 13.55, and 14.3 μ ; nmr (cyclopentane, relative integrals given as the second item in parentheses) τ 2.7 (m, <0.13, arom), 3.3–3.6 (m, 2.42, diazo reactant), 3.7–4.1 (m, 2.64, diazo reactant), 4.2–4.3 (two shoulders, 0.8, heptafulvene), 4.3 (s, 0.96, cyclooctatetraene), 4.3–4.6 (m, 1.13, heptafulvene), 4.83 (d of d, 2.13, J = 9 Hz split by 5.5 Hz, diazo reactant), 5.66 (s, 0.56, heptafulvene ==CH₂), 6.4 (d, 1.0, J = 5.5 Hz, diazo reactant), 6.7–6.85 (m, 1.0), spectrum above τ

7.1 obscured by solvent; uv-visible λ_{max} (cyclopentane) (absorbance given) 224 (A 2200), 254 (A 1200), 265 (A 1120), 276 (A 920), 375 (min, A 12.5), 395 (A 13), 416 (A 12.4), 450 (A 10.0), 488 (A 5.6), 530 (A 2.0), and 578 nm (A 0.6). Analysis by nmr using *p*-dibromobenzene internal standard determined the presence of 3.26 mmol (47%) of 7-cycloheptatrienyldiazomethane, 0.39 mmol (6.5%) of cyclooctatetraene, 0.913 mmol (15.2%) of heptafulvene, plus 0.07 mmol (1.1%) of benzene.

The low-pressure distillate which was collected at -78° had no $4.8 \cdot \mu$ diazo absorption and gave the following uv-visible spectrum: λ_{max} (cyclopentane) (absorbance given) 224 (inflection point, A 14.4), 232 (a 11.0), 242 (A 9.2), 254 (A 8.8), 265 (A 8.6), 278 (A 8.4), 283 (A 7.8), 295 (A 6.4), 350 (min, A 0.12), 372 (A 0.164), 392 (A 0.192), 415 (A 0.20), 450 (A 0.156), 488 (A 0.084), 528 (A 0.04), and 575 nm (A 0.01). The positions of the maxima and minima coincided exactly with those of authentic heptafulvene and the use of ϵ (426 nm) = 484 indicated the presence of 0.146 mmol (2.43%). Analysis on vpc column A at 90° showed the solution contained benzene (0.14 mmol, 2.3%), cyclooctatetraene (0.11 mmol, 1.83%), and a compound of intermediate retention time in a quantity similar to cyclooctatetraene; total recovery was 76.3%.

Heptafulvene was derivatized by adding 0.01 ml of dimethyl acetylenedicarboxylate to 400 ml of the distillate. After several days at 0° the cyclopentane solvent was removed and the residue taken up in 50 ml of benzene. Palladium (10%) on carbon (0.2 g) was added to the solution and air bubbled through it for 20 hr. After evaporation the 0.1384 g of light purple residue was chromatographed on a 1.5×15 cm column of deactivated alumina slurry packed in ether. Elution in 5-ml fractions gave: fractions 1–17, ether, nil; fractions 18–23, ether, 4.6 mg of purple oil; fractions 24–30, ether, nil. The uv-visible spectrum of the purple oil matched that of the heptafulvene derivative described by Doering.²

Photolysis of 7-Cycloheptatrienyldiazomethane at -70° . A 0.45-ml cyclopentane solution containing 0.096 mmol (nmr analysis) of 7-cycloheptatrienyldiazomethane was placed in an nmr tube which was cooled to -70° by a stream of cold nitrogen. The tube was mounted parallel to a quartz immersion well containing a 450-W medium-pressure Hanovia mercury lamp. Filter solution A (transmission above 410 nm) was circulated through the well and photolysis was carried out through a Pyrex filter for 4.6 hr. The nmr spectrum taken immediately at -70° and a spectrum of the same sample plus *p*-dibromobenzene internal standard indicated the presence of 7-cycloheptatrienyldiazomethane (0.082 mmol, 85%), cyclooctatetrane (0.0052 mmol, 5.4%), heptafulvene (0.0073 mmol, 7.6%), and benzene (0.0018 mmol, 1.8%). A control sample at -78° showed no reaction.

Benzophenone-Sensitized Photolysis of 7-Cycloheptatrienyldiazomethane. A 522-ml cyclopentane solution containing 1.74 mmol (nitrogen evolution and nmr analyses) of 7-cycloheptatrienyldiazomethane and 10.00 g (54.9 mmol) of benzophenone was purged with nitrogen for 10 hr (4.85- μ diazo peak undiminished) and then irradiated through filter solution B (transmission 275-373 nm) and Pyrex at 0° with a 450-W Hanovia medium-pressure uv lamp. The photolysis was stopped after 40 min when the $4.85-\mu$ diazo peak had decreased by 82%. The uv-visible spectrum of the photolyzed solution showed no heptafulvene,²¹ though 1.0% would have been detected. The photolysate was distilled through a 0.75 \times 18 inch stainless steel helipak column to give 450 ml of pure solvent (vpc analysis). The residue was bulb-to-bulb distilled (0.8 mm) and the procedure of dissolving the residue in 25 ml of ether and bulb-to-bulb distilling was repeated six times. The original bulb-to-bulb distillate, the combined ether distillates, and the final benzophenone residue were analyzed separately by vpc at 85° on column A. The initial bulb-to-bulb distillate and the combined ether bulb-to-bulb distillate contained benzene (0.139 and 0.028 mmol, respectively (9.6%)). These two solutions also contained an unidentified saturated compound which was eluted just after cyclooctatetraene on vpc (4.9% by weight, assuming detectorresponse linearity with weight). Four minor unidentified substances eluting second, third, forth, and seventh from vpc column A were also contained in the two bulb-to-bulb distallates (3.1%) by weight). Cyclooctatetraene was in all three solutions tested (0.0276, 0.075, and 0.62 mmol) with most of the 9.5% observed found in the final benzophenone residue. Preparative vpc at 80% on column B and subsequent nmr spectra verified the assignments of the first (benzene), fourth (cyclooctatetraene), and fifth (unidentified saturated compound) substances eluted.

Copper-Bronze-Catalyzed Reaction of 7-Cycloheptatrienyldiazomethane. A 21.0-ml cyclopentane solution containing 4.4 mmol (nitrogen evolution analysis) of 7-cycloheptatrienyldiazomethane was added to 25 ml of stirred paraffin oil (American Oil Co., No. 31 USP) at 0°. Cyclopentane (21 ml, pure by nmr analysis) was removed at 0° (1.0 mm). The clear yellow 7-cycloheptatrienyl-diazomethane solution was maintained at 0° as the receiver containing 0.40 ml of deuteriochloroform was cooled to 77°K and the pressure was reduced to and maintained at 1.20–1.4 mm. The addition of copper-bronze (Leo Uhlfelder Co., No. 16 natural copper) without venting the system caused moderate evolution of gas for 30 sec after which a smooth slurry was present. The temperature was slowly increased to 25° where the slurry evolved gas for 10 min and some material collected in the 77°K receiver tube. The slurry was heated to 188° during 40 min when material had collected in the receiver.

Analysis of products by nmr at -58° determined the presence of benzene (0.62 mmol, 14%), cyclooctatetraene (0.81 mmol, 18.5%), heptafulvene (0.009 mmol, 0.22%), cycloheptatrienyl dimer, and/or ether collected also in the 95° decomposition (three-peak m at τ 6.7, 2.4%), cyclopentane, unidentified compound(s) responsible for broad weak m at 8.75 and 9.13, and a compound (0.33 mmol, 7.6% if acetylene) giving a sharp singlet at 8.14. Gas was evolved when the sample was warmed to -7.5° and the τ 8.14 peak decreased by 52%. After 78 hr at -78° the τ 8.14 peak was gone and one had appeared at 8.26 (acetylene). The uv-visible spectrum showed a cyclooctatetraene tail, benzene fine structure from 235 to 260 nm, and very slight maxima at 490 and 527 nm due to heptafulvene. The ir confirmed the presence of benzene and cyclooctatetraene.

The copper slurry residue was diluted with ether, filtered through Celite, and pumped to give a clear solution which had no vinyl absorptions in the nmr.

Low-Temperature Copper-Bronze-Catalyzed Reaction of 7-Cycloheptatrienyldiazomethane. A 2.15-ml cyclopentane solution con-taining 0.169 mmol (nmr analysis) of 7-cycloheptatrienyldiazomethane was cooled to -78° and the pressure was reduced to 3.0 mm for 20 min. Copper-bronze (0.477 g, Leo Unlfelder Co., No. 16 natural copper) was added without venting the system to form a smooth slurry (no evident reaction). The slurry was warmed slowly and at -20° it began to bubble. After a moment the evolution subsided and the flask was warmed to 0° where the cyclopentane and products distilled to the 77°K receiver within 1 min. No further material distilled at 0.95 mm and 25°. The redorange solid received melted at -78° and gave the following nmr data: nmr (-60°, cyclopentane) τ 2.78 (s, 1.03 H, arom), 3.4 (m, 0.56 H), 3.9 (m, 0.44 H), 4.36 (s, 2.00 H, cyclooctatetraene), 4.5-4.8 (m, 0.8 H, heptafulvene 2 and 5 protons), 5.72 (s, 0.67 H, heptafulvene = CH₂), 6.51 (s, 0.45 H, solvent impurity), and 7.3-10.0 (solvent absorption). Analysis (nmr with p-dibromobenzene internal standard) gave: benzene, 0.022 mmol (13.0%); cyclooctatraene, 0.035 mmol (20.7%); heptafulvene, 0.047 mmol (27.8%); and reactant, 0.028 mmol (16.5%); the limit of detection, 8%; total recovery 78%.

Reaction of 7-Cycloheptatrienyldiazomethane Catalyzed by Bis-(benzonitrile)palladium Dichloride. A 13.5-ml cyclopentane solution containing 0.515 mmol (nitrogen evolution analysis) of 7-cycloheptatrienyldiazomethane was stirred with 0.197 g (0.515 mmol) of bis(benzonitrile)palladium dichloride¹⁹ for 20 hr at 0° in the dark

under nitrogen. The resulting slurry was filtered to give 0.185 g of yellow-brown powder which blackened at 220°, but which did not melt. An ir (KBr) spectrum showed only peaks present in bis-(benzonitrile)palladium dichloride (mp 116-118°), but with greatly reduced intensity. The clear filtrate was analyzed by nmr (p-dibromobenzene as internal standard) and contained cycloocta-tetraene (0.24 mmol, 46.7%), benzene (0.18 mmol, 35.0%), and benzonitrile (0.23 mmol). The filtrate was distilled to leave 1.0 ml of solution with ir absorptions identical with authentic benzonitrile and cyclooctatetraene in cyclopentane. The distillate had one nmr peak which coincided exactly with added benzene. The 1.0 ml of residue was evaporated to leave 15 mg (<2.4%) of yellow oil with the nmr spectrum of cycloheptatrienyl compounds and an ir spectrum indicating the presence of carbonyl and alcoholic compounds. Bis(benzonitrile)palladium dichloride released no benzonitrile when stirred at 0° in cyclopentane for 20 hr in a control experiment.

Zinc Chloride Catalyzed Reaction of 7-Cycloheptatrienyldiazomethane in Triglyme. A 22.3-ml cyclopentane solution containing 2.3 mmol (nitrogen evolution and nmr analyses) of 7-cycloheptatrienyldiazomethane was added to 20 ml of distilled triglyme at 0°. Cyclopentane (pure by nmr analysis) was removed at 0.5 mm. A smooth white slurry (5.0 ml) prepared by stirring 10 g of zinc chloride and 25 ml of triglyme was added to the stirred 0° diazo solution. Immediately the slurry bubbled vigorously and its color changed from dark to light yellow. Evolution stopped after 10 min at 0° (1.0 mm) and complete decomposition was verified (ir 4.85- μ peak) after 20 min during which time some product collected in the 77°K receiver. Additional yellow oil was collected as the (0.45-0.7 mm) system was heated to 55°; however, little more was trapped during a 20-min 60-80° triglyme reflux period. The contents of the 77°K receiver were taken up in about 0.5 ml of tetramethylsilane at -78° and analyzed by nmr at -18.5° and later at 35° with added *p*-dibromobenzene. The three peaks not present in a blank run indicated the presence of benzene (0.52 mmol, 22.6%), cyclooctatetraene (0.53 mmol, 23%), and acetylene (0.145 mmol, 6.3%). The acetylene singlet at τ 8.26 decreased by 60% upon warming with evident gas evolution to 35° and disappeared shortly thereafter. The room temperature ir confirmed the presence of benzene and cyclooctatetraene.

The triglyme-zinc chloride slurry was diluted with water and pentane extracted (three 50-ml portions). After six 50-ml water washings the dried organic phase gave 0.0999 g of oil with the following spectra: ir (CCl₄) 3.3, 3.4 (str), 3.49, 5.8 (br, w), 6.63, 6.8, 6.9 (sh), 7.3 (w), 8.13, 9.0 (br str), 9.38, 9.96 and 14.3 μ (str, br); nmr (CCl₄) (relative integral given as second item in parentheses) τ 2.7-2.9 (m, 0.72), 3.3 (s, 0.41, in triglyme), 3.3-3.75 (m, 1.6), 3.75-4.3 (m, 2.0), 4.33 (s, 0.23, cyclooctatetraene), 4.5-5.1 (m, 2.0), 6.3 (s, 0.59, triglyme), 6.3-6.7 (m, 3.5, triglyme), 6.8-8.5 (extremely broad m, 4.6), 8.75 (s, 3.2), 8.87 (s, 1.3), 8.97 (s, 0.95), 9.1-9.3 (m, 1.1). Added *p*-dibromobenzene indicated the presence of 0.23 mmol (10.0%) of cycloheptatrienyl compound; total recovery 55.6%.

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