inadequate and/or isolated electronic states of the molecular ion may intervene.

Experimental Section

Preparation of Phenyl Benzyl Ethers. The amino- and formyl-substituted ethers were commercially available. The others were prepared by heating the appropriate phenol with benzyl chloride and potassium hydroxide[15-17] or potassium carbonate.[18] All samples were purified by recrystallization and their purity confirmed by melting point determination (Table III).

All mass spectra were determined on an AEI MS9 instrument operating at 20 eV (unless otherwise stated) and a source temperature of 200–220°. The trap current was 90 μA. Samples were introduced through a heated inlet system, with the exception of the *m*- and *p*-OH, and *m*- and *p*-NH_2 isomers, which were introduced *via* the direct inlet system. Ionization and appearance potentials were determined by the semilogarithmic plot method.[19]

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(15) W. Staedel, *Ann.*, **217**, 40 (1883).

(16) E. Klarmann, L. W. Gatyas, and V. A. Shternov, *J. Am. Chem. Soc.*, **53**, 3397 (1931).

(17) L. Spiegel and S. Sabbath, *Chem. Ber.*, **34**, 1935 (1901).

(18) F. B. Kipping and J. J. Wren, *J. Chem. Soc.*, 3246 (1957).

(19) See, for example, C. Lifschitz, E. D. Bergmann, and B. Pullmann, *Tetrahedron Letters*, 4583 (1967).

Stability of Molecules Containing Nonalternant Rings

C. F. Wilcox, Jr.

Contribution from the Department of Chemistry, Cornell University,
Ithaca, New York. *Received December 14, 1968*

Abstract: The symbolic analysis of the Hückel molecular orbital properties developed by Dewar and Longuet-Higgins is extended to nonalternant molecules. A simple graph method is described and applied to several representative π systems.

In a recent paper[1] molecules containing single and fused 4*n* rings were treated in terms of the Longuet-Higgins and Dewar analysis of resonance formalism.[2] Their analysis had demonstrated that resonance language when modified to include an algebraic sign for each structure has firm roots in molecular orbital theory and is, as pointed out by Heilbronner,[3] only indirectly related to valance bond theory. It had been shown that molecules composed only of rings of $4n + 2$ π atoms or chains of π atoms have resonance structures with the same algebraic sign so that for these compounds the usual naive resonance structure counting rules apply. With molecules containing one or more 4*n* rings both positive and negative structures occur and this leads to quite different structure counting rules. Modified rules for a number of simple situations have been summarized and exemplified.[1] The present paper extends this approach to molecules containing odd-membered rings (nonalternants) and describes structure counting rules that can be used to correlate Hückel calculations and to estimate relative stabilities. This extension is timely because of the current general interest in nonalternant hydrocarbons. As with the earlier application to alternant hydrocarbons the resonance structure formulation does not give any information not available from an HMO calculation but it does provide a symbolism that permits the chemist to think graphically and thereby hopefully to conceive structures that might otherwise be overlooked from a purely numerical computerized examination.

The earlier conclusions about relative stability of alternant hydrocarbons[2] have two parts that must now be distinguished. The first, that molecules with a zero algebraic sum of structures have triplet Hückel ground states, applies only to alternant species because it depends on the existence of the pairing rule of energy levels. There does not appear to be a simple, rigorous way to extend this to nonalternants. The second conclusion, which was that the relative stability of isomeric hydrocarbons is proportional to the algebraic sum of signed structures, is strictly applicable only to alternant species; however, with slight modification it can be easily applied to nonalternant hydrocarbons as well.

Review of Theory for Alternant Systems. In order to explain the modified rule and its application it is useful to first outline those parts of the alternant hydrocarbon analysis that bear directly. The emphasis here is on the secular determinant in which all of the diagonal terms are set to zero since it can be shown that the numerical value of this determinant is equal to the product of the related eigenvalues.[2] With alternant molecules the contributing π atoms are divided into two classes, starred and nonstarred.[4] By definition no two starred atoms

$$\Delta = \begin{array}{c} \left|\begin{array}{c|c} 0 & A \\ \hline A^{\mathrm{T}} & 0 \end{array}\right| \begin{array}{l} \}\,n \\ \}\,n \end{array} \\ \underbrace{\quad}_{n}\;\underbrace{\quad}_{n} \end{array} \qquad (1)$$

or two nonstarred atoms are adjacent. If the *n* atoms of one class are numbered sequentially followed by the *n* atoms of the second class, the resulting topological determinant[5] of order 2*n* will have the block form shown

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(1) C. F. Wilcox, Jr., *Tetrahedron Letters*, 795 (1968).

(2) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A214**, 482 (1952).

(3) E. Heilbronner, "Molecular Orbitals in Chemistry, Physics and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 329.

(4) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 1931 (1940); C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A195**, 188 (1948).

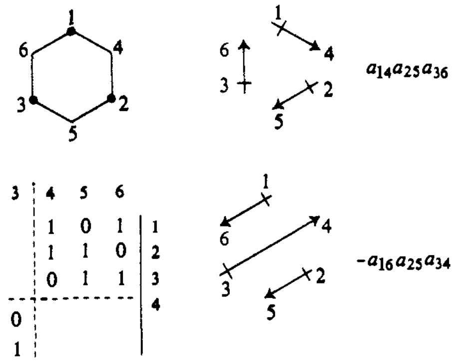
(5) K. Rudenberg, *J. Chem. Phys.*, **34**, 1884 (1961), and references cited therein.

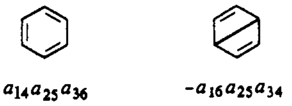
in eq 1. By the property of block determinants[5] and the fact that the determinant of the transpose of a (1) matrix is identical with the determinant of the matrix, the value of Δ is given by eq 2.

$$\Delta = (-1)^n|A|\cdot|A^{T}| = (-1)^n|A|^2 \qquad (2)$$

The crux of the Longuet-Higgins–Dewar analysis is the evaluation of $|A|$ by suitable counting of resonance symbols instead of by conventional methods. By definition[6] the value of a determinant is $\Sigma \pm a_{1_\alpha}a_{2_\beta}\ldots a_{n_\gamma}$ where the summation extends over all permutations of α, β, . . ., γ and the sign is determined by the parity of the permutation. Since each row and column index appears once (and only once) in each of the $n!$ terms of the expanded determinant, each term can be represented by a symbol showing the row and column indices. In Chart I below is shown the alternant π system for benzene, the upper right-hand 3 × 3 block of the blocked secular determinant, and two of the six terms of the expansion with the corresponding symbols. In these symbols the coefficient a_{14} is represented by a vector drawn from atom 1 (row index) to atom 4 (column index). With alternant hydrocarbons there is no need to distinguish between the row and column indices so that resonance structure symbolism conveys sufficient information. A long arrow (or bond) corresponds to a pair of nonadjacent atoms and thus to the Hückel approximation represents a term in the secular determinant that is zero. Such "structures" make no contribution to the expansion of the determinant. It is easy to see that for benzene there are only two nonzero terms (both have the same parity and hence the same sign) in the expansion corresponding to the two Kekulé structures. From eq 2 it follows correctly[7] that the product of the HMO π levels is $(-1)^3\cdot 2^2 = -4$.

Chart I





For molecules containing only chains or rings of $4n + 2$ atoms the parities are always identical[2] and $|A|$ is consequently equal to the number of different Kekulé structures. With molecules containing simple or fused $4n$ rings the parities and signs are mixed but useful rules can be derived.[1]

This completes the review of the treatment of alternant systems, but before extending the method to nonalternants the qualitative usefulness of Δ needs to be emphasized. Visual inspection of HMO energy level diagrams suggests a fairly uniform spread of levels. It follows that for two isomeric hydrocarbons the one with the smaller |Δ| (corresponding to the smaller product of energy levels) will tend to have one or more energy levels closer to zero. Since the approach of levels to a nonbonding state also represents an increasing tendency for easy oxidation or reduction, a small |Δ| can be associated with chemical instability.[8] An alternate statement of this point is that isomers with smaller Δ values will tend to distort geometrically to give molecules containing one or more localized double bonds. These molecules with their olefinic character are more prone to chemical attack. However stated, examples of isomeric hydrocarbons with differing Δ's corresponding to related differences in reactivity come readily to mind.

Nonalternant Molecules. In extending the structure counting approach to nonalternant hydrocarbons it is convenient to classify the molecules according to the number and type of nonalternant bonds present. Those molecules containing only a single nonalternant bond are the simplest to treat since the topological determinant has the block form shown in eq 3.

$$\Delta = \left|\begin{array}{c|c} \begin{matrix}0 & 1 & \cdots\\ 1 & 0 & \\ \vdots & & \end{matrix} & A \\ \hline A^{T} & 0 \end{array}\right| \qquad (3)$$

Except for the pair of elements in the upper left-hand block this determinant is identical term by term with the topological determinant for the corresponding alternant hydrocarbon derived by cleavage of the nonalternant bond. As with the simpler block determinants of the form shown in eq 1, block determinants of the form in eq 4 also have the value $\Delta = (-1)^n|A|\cdot|B|$. It follows

$$\Delta = \left|\begin{array}{c|c} C & A \\ \hline B & 0 \end{array}\right| = (-1)^n\left|A\right|\cdot\left|B\right| \qquad (4)$$

that even nonalternant molecules containing one nonalternant bond have a product of HMO energy levels identical with the corresponding alternant hydrocarbon. Two well-known examples are pentalene and azulene. Pentalene by its relation to cyclooctatetraene has a $\pi_\varepsilon = 0$ from which it follows correctly[7] that HMO pentalene must possess at least one energy level at zero. Using the arguments cited earlier this confers instability on the molecule. By contrast azulene is related to naphthalene and has a $\pi_\varepsilon = -4.0$ which is identical with the π_ε of cyclodecapentane even though there are no coincidences in the energy levels. This approach can be generalized for the parent ring systems as shown in Chart II. In this diagram M and N represent the number of π atoms in each ring. For such simple systems it follows directly that a Hückel-like

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(6) A. C. Aitken, "Determinants and Matrices," 9th ed, Interscience Publishers, Inc., New York, N. Y., 1956.

(7) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, N. Y., 1965; E. Heilbronner and P. A. Straub, "Hückel Molecular Orbitals, HMO," Springer-Verlag, Berlin, 1966.

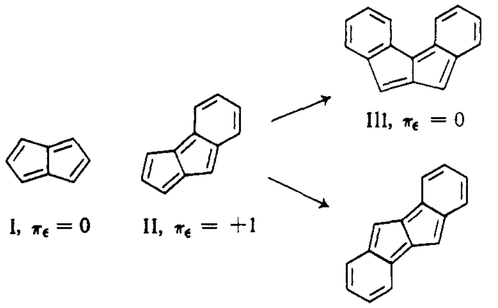
(8) J. B. Bush, cited in ref 7, p 290.

Chart II

M,N (both odd)

$$\pi_\epsilon = \Delta = 2[(-1)^{\frac{(M+N-2)}{2}} - 1]$$

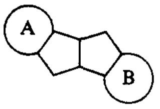
$4n + 2$ rule applies;[9,10] however, for more complex molecules in which aromatic groups have been fused to these basic structures it can happen that $4n$ systems may have surprisingly large π_ε's. The hydrocarbons I–IV given below illustrate the possible change in π_ε from successive fusion of benzo groups. Attention is drawn to the striking difference between the "*trans*"- and "*cis*"-fused molecules.



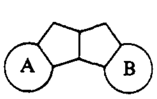
I, $\pi_\epsilon = 0$ II, $\pi_\epsilon = +1$ III, $\pi_\epsilon = 0$ IV, $\pi_\epsilon = +9$

Because of the general interest in the pentalene ring system, the treatment of them will be elaborated a bit further. By suitable manipulation of the algebraic structures of the substituted pentalenes the generalization shown below in Chart III can be derived readily. In these expressions A_D and B_D refer to the number of Kekulé's structures of the separate A and B rings that have a formal double bond at the fusion position. A_T is the total number of Kekulé's structures so that the ratio A_D/A_T and B_D/B_T are the Pauling bond orders of the separate aromatic fragments before fusion. It follows that pentalene derivative with *trans*-fused aromatic fragments will not have a zero HMO energy level if either fragment has any Pauling double-bond character at the fusion position. For the *cis*-fused derivatives there will be a zero HMO level if the double-bond order is the same. This will occur most commonly when the two fused fragments are the same. An example of identical bond orders with different fragments is the hydrocarbon V, which does in fact have a zero HMO level. It is also worth noting that the present approach makes a distinction between isomers that is not made by the more conventional perimeter rule.[11] The two dibenzopentalenes are good examples of the different predictions.

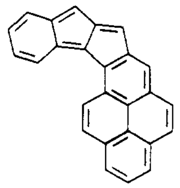
Chart III



$$\pi^\varepsilon = (A_TB_T - A_DB_D)^2 = 0 \text{ when } \left(\frac{A_D}{A_T}\right)\left(\frac{B_D}{B_T}\right) = 1$$

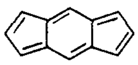


$$\pi_\varepsilon = (A_TB_D - A_DB_T)^2 = 0 \text{ when } \frac{A_D}{A_T} = \frac{B_D}{B_T}$$



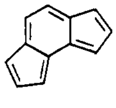
V, $\pi_\epsilon = 0$

Those nonalternant molecules containing two or more nonalternant bonds that are of the same class (*i.e.*, either all between starred atoms or all between unstarred atoms) because of eq 4 can be treated exactly like the molecules with a single nonalternant bond and the product of their HMO energy levels is also given by eq 2. One example of such a molecule is VI for which the observed HMO zero-energy level is correctly predicted. An interesting generalization about the relative stability of molecules like VI will be presented at the end of this paper.

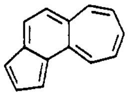


VI, $\pi_\epsilon = 0$

The final set of molecules to be considered here are those nonalternants containing two nonalternant bonds that belong to different classes. Hydrocarbons VII and VIII are simple examples. For such molecules the topological determinant will, with suitable numbering, be of the form in eq 5. The $n!$ terms in the expansion



VII



VIII

$$\Delta = \left|\begin{array}{c|c} \begin{matrix}0&1&\cdots\\1&0&\\\vdots&&\end{matrix} & A \\ \hline A^T & \begin{matrix}0&1&\cdots\\1&0&\\\vdots&&\end{matrix}\end{array}\right| \tag{5}$$

of (5) can be conveniently grouped into two sets that either (a) contain no elements from either the upper left-hand block or the lower right-hand block or (b) contain at least one element from either of these main diagonal blocks. The contribution to Δ from the a terms is identical with the value of the corresponding alternant hydrocarbon in which both nonalternant bonds have been cleaved (eq 2). The contributions to Δ from the b terms are readily calculated but a new symbolism is required. Since the b terms come from the full determinant rather than one $n \times n$ block, each atom of the molecule must be represented once as a row element and once as a column element. In terms of the vector notation employed earlier in Chart I a vector

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(9) Those species in which $(M + N - 2)/2$ is odd represents the largest π_ε so that for these $(M + N - 2)/2 = 2n + 1$ or $M + N - 2 = 4n + 2$; however, $M + N - 2$ is just the number of π atoms in the molecule.

(10) The same conclusion can be reached by perturbation methods: M. J. S. Dewar, *J. Am. Chem. Soc.*, 74, 3345 (1952); M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 1617 (1954); D. Peter, *ibid.*, 1023 (1958); K. Fukui, A. Imamura, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Japan*, 33, 1591 (1960).

(11) A. Streitwieser, "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961.

must originate at each atom and another must terminate at it. As with alternate molecules and the Kekulé symbols used to represent terms in the topological determinant, long arrows represent β_{ij} elements between nonadjacent atoms and thus in the Hückel approximation give terms making no contribution to Δ. The first step in determining the contributing b terms is to write down all arrow diagrams in which at least one of the nonalternant bonds is represented by an arrow. No regard is given to the direction of the arrow except that dictated by the requirement that each atom must be attached to one head and to one tail. The various diagrams will contain one or more islands defined by the cyclic flow of arrows. For each diagram the algebraic sign of the term it represents is the product of factors obtained by assigning each island containing an odd number of atoms a factor of $+1$ and each island containing an even number of atoms a factor of -1.

The procedure sounds difficult but after a few trials it becomes easy. The a and b contributions for molecules VII are shown below in Chart IV. This analysis correctly predicts that the product of HMO energies is -8.

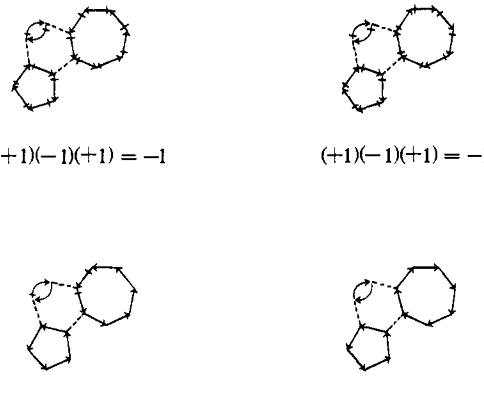
Chart IV. Analysis of Hydrocarbon VIII, $C_{14}H_{10}$

a—contributions

+1 +1

$$\Delta_a = (-1)^7(2)^2 = -4$$

b—contributions



$(+1)(-1)(+1) = -1$ $(+1)(-1)(+1) = -1$

$(+1)(-1)(+1) = -1$ $(+1)(-1)(+1) = -1$

$$\Delta_b = (-1) + (-1) + (-1) + (-1) = -4$$

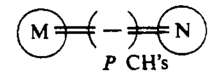
$$\Delta = \Delta_a + \Delta_b = -8$$

Following this procedure it is possible to develop the correlative generalizations shown in Chart V.

It can be seen that molecules of the A type in Chart V cannot have a zero HMO level. Also, the stability as judged by π_ε is independent of the number of connecting methylenes. Lastly, those examples in which $M + N = 4n$ should be less reactive than those in which $M + N = 4n + 2$. Because of the lack of restriction of P the total number of π atoms in the most stable molecules can be either $4n$ or $(4n + 2)$.

Chart V

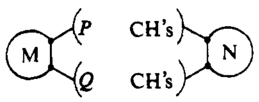
A



M and N odd, P even

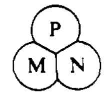
$$\pi_\varepsilon = (-1)^{P/2}[4 + (-1)^{(M+N)/2}] \quad (6)$$

B



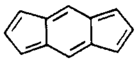
$$\begin{aligned}\pi_\varepsilon = \; & 2(-1)^{\text{no. of dbl bonds in molecule}} \\ & -2(-1)^{\text{no. of dbl bonds in center ring}} \times [1 + (-1)^P] \\ & -2\end{aligned} \quad (7)$$

M and N odd; P and Q either both even or both odd

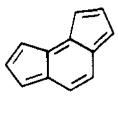


$$\begin{aligned}\pi_\varepsilon = \; & 3(-1)^{\text{no. of dbl bonds in molecule}} \\ & +2(-1)^{\text{no. of dbl bonds in M}} \\ & +2(-1)^{\text{no. of dbl bonds in N}} \\ & +2(-1)^{\text{no. of dbl bonds in P}}\end{aligned} \quad (8)$$

Molecules falling into group B of the diagram are quite varied. One obvious way to have HMO instability is to have an even number of double bonds in the molecule combined with an odd number of intervening methylene groups in the branches joining M and N. An example is hydrocarbon IX for which the product of the HMO levels is zero.[7] This is to be contrasted with the isomer X in which both the P and Q branches have an even number of methylenes and for which the product of the HMO levels is[7] -4 as required by eq 7.

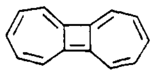


IX



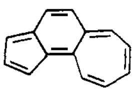
X

The second way in which hydrocarbons of type B can have a zero HMO level is to possess an odd number of double bonds in the whole molecule and an odd number of formal double bonds in the central ring combined with an even number of methylene groups in either of the branches joining M and N. An example is hydrocarbon XI. Clearly the least stable molecules of type B can have either $4n$ or $(4n + 2)$ π atoms.



XI

Equation 7 requires that the maximum value for $|\pi_\varepsilon|$ will arise when there is an odd number of double bonds in the molecule combined with an even number of formal double bonds in the central ring and even P and Q branches. An example is hydrocarbon XII for which eq 7 correctly predicts that the product of the HMO levels is -8.0.



XII, $\pi_\varepsilon = -8$

By suitable manipulation of the algebraic equivalents of the preceding paragraph it is readily seen that the most stable hydrocarbon of type B will have a $4n + 2$ central ring flanked by two rings, the sum of whose sizes is $4n'$. In addition the flanking rings will be fused to the central rings so as to form even bridges, which for a central benzene ring means *meta* fusion.

The group of molecules of type C in Chart V can be seen to be incapable of having a zero HMO level because only one of the coefficients is odd and must enter as ± 3 to the final value of π_ε. It might be supposed that the least stable molecules would occur when the first two terms of eq 8 had one sign and the last two terms have the opposite sign ($\pi_\varepsilon = \pm 1$). It is demonstrated in the Appendix that this situation is topologically impossible. The most stable molecule should occur when all of the terms in eq 8 have the same sign ($\pi_\varepsilon = +9$). Using the same method applied above and described in the Appendix it is possible to show that this maximum value is also topologically impossible. Accordingly, neither of the extreme values are represented by real molecules.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

Appendix

The total number of π atoms in a molecule of type C of Chart V is $(M + N + P - 4)$ and the total number of double bonds in the molecule is $(M + N + P - 4)/2$. For the case where M, N, and P are all odd the number of double bonds in each is $(M - 1)/2$, $(N - 1)/2$, and $(P - 1)/2$, respectively. If the total number of double bonds and the number of double bonds in one ring, say M, are to be even it follows that $[(M + N + P - 4)/2] - [(M - 1)/2] = \text{even} - \text{even} = \text{even}$ so that $N + P - 3$ must also be even. This is clearly impossible for odd N and P and no cases of type C with a $|\pi_\varepsilon|$ of 1 can exist with an even total number of double bonds. If the total number of double bonds and the number of double bonds in one ring, say M, are to be odd it follows that $N + P - 3$ must be even. Again this is impossible and no examples of type C with $\pi_\varepsilon = \pm 1$ can exist.

The Kinetics of the Reaction of Ethyl Diphenylphosphinate with Phenylmagnesium Bromide

H. R. Hays

Contribution from The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. *Received August 30, 1968*

Abstract: The reaction of ethyl diphenylphosphinate and phenylmagnesium bromide has been investigated in tetrahydrofuran (THF). Infrared and phosphorus nmr spectral evidence has been obtained for the rapid formation of a moderately strong 1:1 complex between the phosphoryl oxygen atom of the phosphinate and the magnesium atom of the Grignard reagent. The K_{eq} for the formation of this complex is estimated to be about 6×10^3 l. mole^{-1} or greater. The exchange of ethyl diphenylphosphinate in the complex is fast on the nmr time scale. Subsequent slow reorganization of this complex to product has been found to follow first-order kinetics and to be concentration independent over the range that was investigated (0.03–0.5 M). Below 0.03 M the results suggest that dissociation of the complex becomes appreciable. The E_a (13.4 kcal/mole) and $\Delta S^{\ddagger}$ (−33.2 eu) for the reorganization of the complex to product were calculated from the average first-order rate constants obtained at four temperatures. The phosphorus nmr spectrum of the product of the reorganization step indicates a relatively strong complex between the phosphoryl oxygen atom of triphenylphosphine oxide and magnesium bromoethoxide and not a pentacovalent phosphorane as has been suggested. Tributylphosphine oxide accelerates the rate of reaction of ethyl diphenylphosphinate with phenylmagnesium bromide, whereas magnesium bromoethoxide retards the reaction. Phosphorus nmr spectral evidence for complex formation is presented. The rate of reaction of ethyl diphenylphosphinate with phenylmagnesium bromide in THF is about five times that in diethyl ether. All of these observations appear consistent with the proposed mechanism. Spectral and kinetic data have been obtained for the more complex reaction of diphenylmagnesium with ethyl diphenylphosphinate.

The kinetics and mechanisms of reactions of Grignard reagents with ketones have been studied extensively.[1] In contrast, the kinetics of the reactions of phosphorus esters with Grignard reagents have received little attention. This may be due in part to the ensuing controversy over the nature of the Grignard reagent and its role in the mechanism of reaction with ketones. Another factor may be that many of the reaction mixtures of phosphorus esters and Grignard reagents become heterogeneous in diethyl ether alone or in benzene–ether mixtures.[2]

During the investigation of the reactions of phosphorus

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(1) For recent pertinent reviews of this work see: (a) E. C. Ashby, *Quart. Rev.* (London), **2**, 259 (1967), and E. C. Ashby, R. B. Duke, and H. M. Neumann, *J. Amer. Chem. Soc.*, **89**, 1964 (1967); (b) S. G. Smith and J. Billet, *ibid.*, **89**, 6948 (1967); (c) S. G. Smith and G. Su, *ibid.*, **88**, 3995 (1966); (d) H. O. House and J. E. Oliver, *J. Org. Chem.*, **33**, 929 (1968); (e) G. E. Coates, M. L. H. Green, and K. Wade in "Organometallic Compounds, Vol. I, The Main Group Elements," G. E. Coates and K. Wade, Ed., Methuen and Co., Ltd., London, EC4, 1967, pp 76–103.

(2) This has been recognized as a complicating factor in rate studies of the reactions of alkyl diphenylphosphinates and methylmagnesium iodide: K. D. Berlin and R. U. Pagilagan, *J. Org. Chem.*, **32**, 129 (1967).