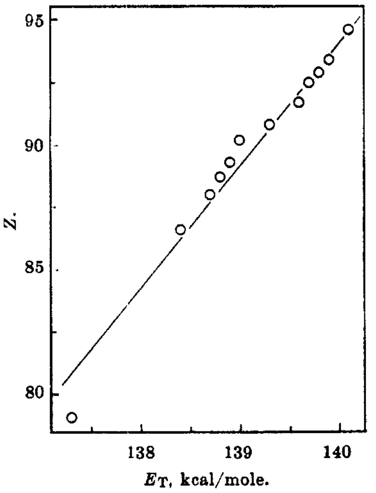


Figure 1.—Plot of ethyl acetate n → π^* transition energy (E_T) vs. solvent polarity constant (Z) in ethanol-water solutions. The least-squares line corresponds to $E_T = 0.202Z + 121$; correlation coefficient = 0.98.

tion energy of ethyl acetate increasing by 4.6 kcal/mole between isooctane and water.[5a] In this respect it is quite similar to the corresponding transitions of many other carbonyl compounds.[6] The similarity of solvent effect on ground- and excited-state heats of solution of ethyl acetate can be interpreted as implying little change in polarity during the n → π^* transition, a conclusion in keeping with the known modest decrease of the unsubstituted carbonyl group dipole moment in the n,π^* state.[7] It also suggests that the solvent–solute hydrogen bond, which several lines of evidence indicate is broken during the electronic transition and is not present in the n,π^* excited state of carbonyl compounds,[6a,8] must play only a minor part in determining the total ground-state heat of solution, and presumably, the total excited-state heat of solution. It also suggests that the degree of "structuredness" of the alcohol–water solvent, which frequently has such a marked effect on $\Delta\bar{H}_S$ values[2,3,9] has a much smaller effect on more intimate types of intermolecular interactions such as hydrogen bonding between a basic center in a molecule and one solvent molecule. On the other hand, the excellent correlation of the n → π^* transition energy of ethyl acetate with Z[10] and Y,[11] empirical solvent polarity parameters (note Table I and Figure 1), indicates that these are good measures of solvent hydrogen-bonding ability.

Experimental Section

Solvents were prepared by mixing appropriate quantities, measured by volume at 25°, of absolute ethanol and distilled water. Reagent grade ethyl acetate was carefully distilled prior to use. The details of measurement of the ester absorption spectra have been described previously.[5a]

Registry No.—Ethyl acetate, 141-78-6.

[6] (a) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 186–188; (b) J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958); (c) E. M. Kosower and G.-S. Wu, *J. Am. Chem. Soc.*, **83**, 3142 (1961).

[7] G. Berthier and J. Serre, "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 49.

[8] M. Ito, K. Inuzuka, and S. Imanishi, *J. Chem. Phys.*, **31**, 1694 (1959).

[9] E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **87**, 1393 (1965).

[10] E. M. Kosower, *ibid.*, **80**, 3253, 3261 (1958).

[11] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 297–312.

A Perturbational Molecular Orbital Method Applied to Competing 1,2- and 1,4-Cycloaddition Reactions

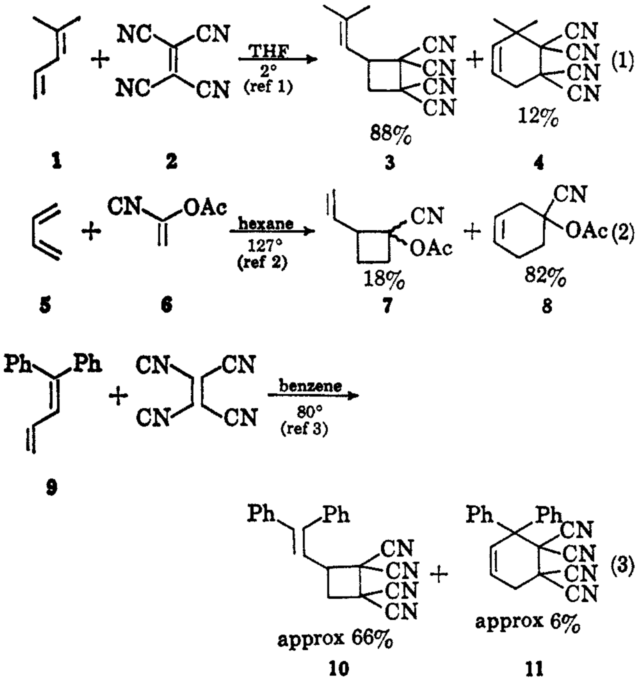
WILLIAM C. HERNDON AND JEROLD FEUER

Department of Chemistry, Texas Technological College, Lubbock, Texas 79409

Received May 26, 1967

Three papers have recently appeared which describe Diels–Alder reactions under mild conditions that yield a cyclobutyl derivative in addition to the normal six-membered ring adduct.[1–5] Typical conditions and yields are outlined below. An important fact which attracts an attempt at a theoretical explanation is the drastic change in the relative yields of the two types of products with differing reactants (Scheme I).

SCHEME I



The commonly accepted mechanism for cyclobutane formation postulates a diradical intermediate.[6] This diradical is also the most easily visualized intermediate for the reported isomerizations, **7** → **8**[3] and **10** → **11**.[7] Therefore a suggested two-step mechanism involving a diradical intermediate, which can lead to either of the two products,[2] seems reasonable for these reactions.

[1] C. A. Stewart, Jr., *J. Am. Chem. Soc.*, **84**, 117 (1962).

[2] J. C. Little, *ibid.*, **87**, 4020 (1965).

[3] J. J. Eisch and G. R. Husk, *J. Org. Chem.*, **31**, 589 (1966).

[4] Two other examples are the reactions of tetrafluoroethylene with cyclopentadiene [J. J. Drysdale, W. W. Gilbert, H. K. Sinclair, and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 245, 3672 (1958)] and the thermal dimerization of butadiene under unusual conditions [H. W. B. Reed, *J. Chem. Soc.*, **685** (1951)]. Schueller has also reported a very small amount of vinylcyclobutane from the reaction of butadiene and ethylene (see ref 5, pp 71–75).

[5] K. E. Schueller, "Cycloaddition Reactions of Ethylene and α-Acetoxyacrylonitrile," Harvard University Press, Cambridge, Mass., 1966, p 29.

[6] J. D. Roberts and C. M. Shorts, *Org. Reactions*, **12**, 1 (1962); R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 779–791.

[7] M. J. Mintz and J. C. Little, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, O-154.

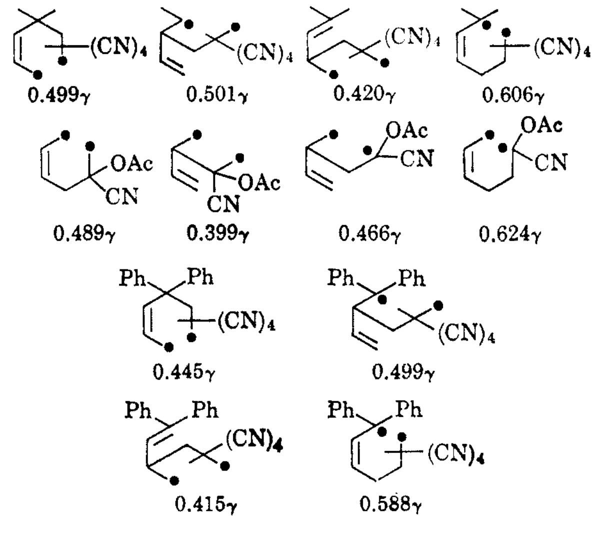
Of course, other mechanistic possibilities can be envisaged. The most obvious would be concerted 4 + 2 cycloaddition[8] to give the usual Diels–Alder adduct and a separate, competing two-step reaction to yield the substituted vinylcyclobutane.[5] In addition, the intermediate in the cyclobutane-forming reaction might be dipolar rather than radicaloid in character.[9] We do regard concerted Diels–Alder reactions as unlikely for reactions 1 and 3 since the dienes cannot assume the necessary *s-cis* conformation,[10] but the two unassociated pathways would be quite possible in reaction 2.

In this note, we address ourselves to the following questions. Can diradical intermediates theoretically account for the observed product distributions, at least semiquantitatively? And if so, would a competing concerted cycloaddition to yield the normal adduct be an admissible side reaction?

To consider these problems, we make use of the perturbational molecular orbital method (PMO) outlined by Dewar,[11] which we have previously applied to some discussions of reactivity in several Diels–Alder reactions.[12-14] In outline, one obtains wave functions (eigenvalues and eigenvectors) for the two separated molecules or radicals which are to react to form a larger molecule. The formation of a new bond or bonds is then considered as a perturbation on the wave functions of the reactants. Simple formulas allow one to calculate the change in energy which occurs upon making the new bond or bonds.[11,12] For consistency, we calculate all perturbation energies to the second order. A calculated difference in energy for two reactions is finally assumed to be equal to RT times the natural log of the relative rates of the two reactions. The advantages of using a perturbational approach to problems of reactivity have often been discussed[11,15-19] and the justification for correlating calculated activation energies with experimental rates of reactions is based on the work of Evans and Polanyi[20] (also, see Dewar[21]).

For reactions 1, 2, and 3 we used the method in the simplest possible form. Hückel-type MO's were determined for the reactant molecules. Coulomb integrals were α(carbon) = α, α(oxygen, one electron) = $\alpha + {}^{3}/_{2}\beta$, α(oxygen, two electrons) = $\alpha + {}^{5}/_{2}\beta$, α(nitrogen, one electron) = $\alpha + {}^{1}/_{2}\beta$, α(saturated carbon, psuedo heteroatom model) = $\alpha + 2\beta$.[22,23] The resonance integrals for carbon–heteroatom bonds were chosen roughly proportional to overlap integrals. β(carbon–oxygen in ester linkage) = 0.64β, β(carbon–oxygen in carbonyl) = 0.88β, β(nitrile) = 1.20β, β(carbon–saturated carbon) = 0.70β. Tables of the resultant eigenfunctions are available upon request. It should be noted that the quantitative nature of the results which are obtained is unchanged upon modest changes in the integral values. Next, accepting that diradicals are produced as the first step in the three reactions, perturbation theory was used to calculate the change in energy which occurs as dienophile attacks diene to give intermediate, for every possible position of attack. The perturbation energies[24] (assumed to reflect a difference in energy in the transition state) are listed below each conceivable intermediate and the results are in accord with chemical intuition and resonance theory. The favored diradical intermediate as predicted by the calculations is in every case the only intermediate which can lead to the observed products (Chart I).

CHART I



The diradical intermediate is now treated as two separate radicals which can combine at either end of the mesomeric allylic system. Perturbation theory is again used to estimate the most likely reaction path. In reactions 1 and 3 the cyclobutane product is preferred by 0.0902 and 0.0927γ, respectively. In reaction 2 the cyclohexene pathway is predicted to be more stable by 0.0782γ. *Thus, the PMO method confirms the inversion of product distribution* and if values of 10–20 kcal/mole are chosen for the perturbation parameter γ, the calculated product distributions are in rough agreement with the experimental results.

Do the combined theoretical and experimental results allow one to exclude 4 + 2 cycloaddition as a competing process for the formation of cyclohexene

---

(8) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(9) Solvent effects in some 1,2-cycloaddition reactions of highly electrophilic olefins to various alkenes certainly suggest that this statement is true. For examples, see ref 1; J. K. Williams, D. W. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962); S. Proskow, H. E. Simmons, and T. L. Cairns, *ibid.*, **88**, 5254 (1966); and C. J. Dempster, "Cycloaddition Reactions of Tetracyanoethylene to 1,3-Dienes," Harvard University Press, Cambridge, Mass., 1967. In contrast, Little[2] found only a small solvent effect on the ratio of products in reaction 2.

(10) A dissent from this view should be noted. A referee has pointed out "that the transition state of such reactions need not follow a picture-book path of high symmetry, but may have complicated geometries. For example, since rotations about single bonds are fast, bond formation may be highly unsymmetrical and begin with the diene near the *s-trans* configuration, but it may be accompanied by rotation, so that the over-all 4 + 2 cycloaddition is concerted."

(11) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).

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

(13) W. C. Herndon and L. H. Hall, *Tetrahedron Letters*, 3095 (1967).

(14) J. Feuer, W. C. Herndon, and L. H. Hall, *Tetrahedron*, in press.

(15) M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 65 (1965).

(16) K. Fukui, "Modern Quantum Chemistry," Part 1, O. Sinanoglu, Ed., Academic Press Inc., New York, N. Y., 1965, p 49.

(17) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

(18) R. F. Hudson and G. Klopman, *Tetrahedron Letters*, 1103 (1967).

(19) G. Klopman and R. F. Hudson, *Theoret. Chim. Acta*, **8**, 165 (1967).

(20) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936).

(21) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956).

(22) A. Liberles, "Introduction to Molecular Orbital Theory," Holt, Rinehart and Winston, Inc., New York, N. Y., 1966, p 169.

(23) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 135.

(24) The perturbation energies are given in terms of a parameter γ which is defined in ref 12 and 14.

product in reaction 2? A kinetic analysis of the proposed reaction scheme can be made as shown. The steady-state hypothesis is invoked for the reactive intermediate I. The ratio of rate constants k_c/k_b is

$$\begin{tikzcd} \mathbf{5} + \mathbf{6} \arrow[r, "a"] \arrow[dr, "d"'] & {[I]} \arrow[r, "b"] \arrow[d, "c"] & \mathbf{7} \\ & \mathbf{8} & \end{tikzcd}$$

$$\mathbf{8}/\mathbf{7} = (k_d/k_a)(k_c/k_b + 1) + (k_c/k_b)$$

given by the work in the previous paragraph, $k_c/k_b = \exp(0.0782\gamma/RT)$. The ratio of products **8**/**7** is known experimentally; the ratio of k_d/k_a can therefore be determined. The appropriate value of γ is that determined from the product distribution in the reaction of 1-cyanovinyl acetate with, perhaps, 1,1-dimethylbutadiene. Since these data are not available, an empirical value of γ determined from the results of reaction 1, $\gamma = 12.0$ kcal/mole, gives $k_d/k_a = 0.29$. So our answer to the second question is that we cannot exclude a simultaneous 4 + 2 cycloaddition reaction as a possibility in the formation of the Diels–Alder adduct. However, more experimental data may resolve this question.

In summary, within the framework of the PMO method, a two-step mechanism with a common intermediate can account for differing ratios of the two types of products in these anomalous Diels–Alder reactions, although some competing cycloaddition may be possible.

We recognize that we have taken a very simplified view of this whole problem. The observation of *cis–trans* isomers in reaction 2[2] and solvent effects have been ignored. The use of a simple Hückel method to compare energies of diverse systems is also difficult to justify theoretically. The justification for this approach must, as usual, be the comparison of the calculations with experimental results.

Acknowledgment.—We would like to thank the staff of the computer center of Texas Technological College for assistance in computing problems and generous gifts of computer time. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (PRF No. 3069-A4). We also wish to thank Dr. K. E. Schueller and Dr. C. J. Dempster who very kindly made copies of their dissertations available to us.

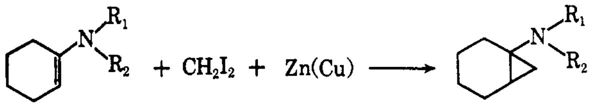
Synthesis and Nuclear Magnetic Resonance Analysis of Cyclopropyl- and 1-Bicyclo[*n*.1.0]alkylamines

D. L. MUCK AND E. R. WILSON

Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

Received July 27, 1967

In connection with other work in these laboratories, we have had a need for a series of 1-aminobicyclo[*n*.1.0]alkanes. A recent report by Blanchard, Simmons, and Taylor[1] described the synthesis of a few of these compounds, although generally in low yield, by methylene addition to enamines using methylene iodide and zinc–copper couple. An earlier report by Wittig and Wingler[2] described a similar addition to an enamine, but these workers used bis(iodomethyl)zinc as the methylene transfer agent. In this paper we would like to report a simple procedure for preparing cyclopropyl- and 1-bicyclo[*n*.1.0]alkylamines in good yields. We have found that enamines readily react with diazomethane in the presence of cuprous chloride to give the corresponding cyclopropyldialkylamines, with yields of 65–80% of distilled products. In the normal procedure, a twofold molar quantity of diazomethane in ether is dripped into a stirred ether solution of the enamine and suspended cuprous chloride at room temperature.



Cuprous salts have been well established in recent years as catalysts in the reaction of diazomethane with olefins to give cyclopropane derivatives[3] and earlier as polymerization catalysts for diazo compounds.[4] One early report by Bawn and Ledwith[4c] concerning new catalysts for polymerization reactions mentioned that an ether solution of cuprous iodide containing a little aliphatic amine gave an intense red color upon the addition of diazoethane, which disappeared as the diazoethane was exhausted by polymerization. It is interesting that in our reactions of cyclopropyl ring formation we also observe an intense red color which disappears with the removal of diazomethane.

In order to demonstrate the generality of the reaction, both the amine and the aldehyde or ketone used to prepare the enamines were varied to give a number of different starting materials. The results of methylene addition to the enamines prepared are shown in Table I. Although there may be a slight steric hindrance to addition in a trisubstituted enamine, the reaction in general was not affected by the nature of the alkyl substituents either on the double bond or on the nitrogen atom. However, when there were no alkyl groups substituted on the double bond, such as with vinylpyrrolidine, an apparent decrease in reactivity was observed and twice as much diazomethane was required as was generally needed.

Interpretation of Nmr Spectra.—Nmr spectra were obtained on all of the compounds prepared and analyzed as much as possible in order to support the proposed structures. The data obtained are listed in Table II, where the *endo* protons are designated as "A"

---

(1) E. P. Blanchard, H. E. Simmons, and J. S. Taylor, *J. Org. Chem.*, **30**, 4321 (1965).

(2) G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2146 (1964).

(3) (a) P. Yates and J. Fugger, *Chem. Ind.* (London), 1511 (1957); (b) M. F. Dull and P. G. Abend, *J. Am. Chem. Soc.*, **81**, 2588 (1959); (c) G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961); (d) W. v. E. Doering and W. Roth, *Tetrahedron*, **19**, 715 (1963); (e) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, 673 (1963); (f) W. R. Roth, *Ann.*, **671**, 10 (1964); (g) R. E. Pincock and J. I. Wells, *J. Org. Chem.*, **29**, 965 (1964).

(4) (a) G. D. Buckley, L. H. Cross, and N. H. Ray, *J. Chem. Soc.*, 2714 (1950); (b) L. C. Leitch, P. E. Gagnon, and A. Cambron, *Can. J. Res.*, **28b**, 256 (1950); (c) C. E. H. Bawn and A. Ledwith, *Chem. Ind.* (London), 1180 (1957).