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THE *cis*-HEXATRIENE ELECTROCYCLIZATION

ATTEMPTED CALCULATION OF THE TRANSITION STATE GEOMETRY

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Abstract—A model has been developed to permit calculation of the energy changes associated with the electrocyclic reaction of *cis*-hexatriene to 1,3-cyclohexadiene. A novel method for solving the problems associated with calculations of the pi system energy and the energy of the forming single bond as the terminal carbons undergo rehybridization was developed. The result permits calculation of the total energy in terms of contributions from the forming sigma bond, the pi system, non-bonded interactions and bond energy changes resulting from rehybridization. The angle of rotation θ about the C_2—C_3 and C_4—C_5 bonds was used as an approximation to the reaction coordinate. Surprisingly the plot of energy *vs* θ showed no maximum for either the disrotatory or the conrotatory stereopath. Failure to produce a transition state was attributed to problems with assignment of a reasonable kcal equivalent to the Hückel β, and an artificial device was proposed to solve the problem. The geometry of the disrotatory transition state achieved in this manner suggests that non-bonded interactions between hydrogens on the terminal carbon are not serious, but the dihedral angle between the p-orbitals at C_2—C_3 (and C_4—C_5) leads to a significant degree of isolation of C_2 and C_5 from the remainder of the pi system.

Of the conconcerted thermal reactions to which conservation of orbital symmetry theory[2] is applied the electrocyclic reaction is of considerable interest, initially because of its importance to vitamin D chemistry[3] and its stereochemistry,[4] and more recently because of its application to the chemistry of α-pyrans[5] and 1,2-dihydropyridines.[6] It is also important as the first molecular example of a disrotatory process. Some years ago we attempted to develop a model for this electrocyclic reaction[7] which would enable us to assess the importance of various chemically significant energy terms at the transition state.

General procedure. Since we desired data about the extent to which various energy terms, that is sigma bond energy, pi system energy, strain energy, etc, contribute to the energy of the transition state, a "total energy" for each conformation of the molecule as it proceeds from *cis*-hexatriene to cyclohexadiene was calculated by a modified Hendrickson procedure.[8] Hendrickson has applied his method only to saturated hydrocarbons, so there arise in the present case a number of novel problems. The most important of these is the calculation of the energy changes which occur as the terminal atoms undergo a rehybridization from sp^2 to sp^3. A large part of the difficulty involves determination of the pi system energy at intervening stages as the triene converts to a diene plus a sigma bond. In our model the method of calculating the energy of the forming sigma bond provides the key to solution of most of the other problems.

Parameters and coordinates. The general coordinate system is illustrated in Fig 1 with respect to the initial conformation of *cis*-hexatriene. The geometric alterations required to convert *cis*-hexatriene to cyclohexadiene are described in terms of two sets of three parameters each. These are θ, a rotation about the axis of the C_2—C_3 or the C_4—C_5 bond; ω, a rotation about the axis of the C_1—C_2 or the C_5—C_6 bond; and η, a rehybridization parameter for carbons one and six which varies from 0 (sp^2) to 1 (sp^3). Rotational angles, θ and ω, are zero for the positions shown in Fig 1 and increase in a positive sense as indicated by the arrows. The rotation θ was taken to represent the reaction coordinate and the total energy was minimized for values of θ from 90°–180° in 15° intervals.

Sigma bond energy. Rehybridization of C_1 and C_6 in terms of η was carried out using an auxiliary pair of coordinate systems. The x′ axis for each auxiliary coordinate system is an extention of the C_1—C_2 or C_5—C_6 bond, the y′ axis is in the plane of the molecule when the conformation is that shown in Fig 1, and the coordinate system is right handed.

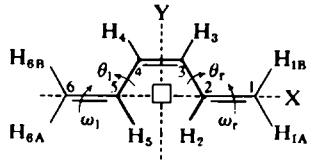


Fig 1. Model for the *cis*-triene and the generalized coordinates.

This coordinate system remains fixed with respect to C_1 or C_6 as rotations θ or ω take place. The S, $P_{x'}$, $P_{y'}$, $P_{z'}$ components of the six bonds at C_1 and C_6 can be written as functions of η in these coordinate systems (Appendix), and the $P_{x'}$, $P_{y'}$, and $P_{z'}$ components were used to define unit vectors (Appendix). The unit vectors for the C—H bonds were multiplied by the C—H bond length while the orbital vector for the orbital used to form the new sigma bond was retained as a unit vector. Transformation cosines for conversion from the auxiliary to the generalized coordinates were determined as functions of θ and ω, so that the coordinates of all entities attached to C_1 and C_6 could be written as functions of θ, ω, and η.

The one-electron orbitals at C_1 and C_6 may interact to form a new bond, which could be represented by a bond integral, $\langle S^{\eta}P^{4-\eta}|H|S^{\eta}P^{4-\eta}\rangle$. In general the bond will have both pi and sigma components, i.e. it will have the character of a triple bond. We dissect the p-contribution to the bond into components along the line of the sigma bond forming between C_1 and C_6 (P_b) and two mutually perpendicular directions ($P_{b'}$ and $P_{b''}$). The sigma bond may then be written as $a_r a_l\langle S|H|S\rangle + (a_l b_r + a_r b_l)\langle S|H|P_b\rangle + b_l b_r\langle P_b|H|P_b\rangle$, where the a_r, a_l, b_r, b_l are functions of the parameters θ, ω, η for the right and left halves of the molecule.

To evaluate the various resonance integrals we have made the assumption that each is proportional to the corresponding Slater overlap integral. This introduces three proportionality constants (C_s, C_{sp} and C_p) which must be evaluated. This was done by using the data of Dewar and Schmeising,[9] who have worked out relations between bond energy and the hybridization of the atoms bonded. Their results give the data of Table 1, from which the three proportionality constants ($C_s = 25$, $C_{sp} = 38{\cdot}4$ and $C_p = 153$) can be determined. The results permit determining the single bond energy in kcal/mole.

Pi system energy. A simple Hückel calculation was used to determine the energy of the pi system. Each interaction between orbitals on adjacent carbons was set equal to some fraction, k_{ij}, of a beta unit. With the exception of k_{34} ($= 1{\cdot}0$), all k_{ij} are functions of the geometry, hence of one or more of the parameters. A simple vector procedure was used to calculate the various k_{ij}. For example, to obtain k_{12} an orbital vector whose length is proportional to the fractional p character of the hybrid orbital was obtained for the orbital at C_1, and a unit vector was set up for the orbital at C_2. The dot product of the two gives k_{12}.

Since the bond between C_1 and C_6 has triple bond character the k_{16} takes into account both $P_{b'}$ and $P_{b''}$ components. The k_{16} must also vary with the distance between C_1 and C_6. This was accomplished by setting the integral $\langle 2P_{b'}|H|2P_{b'}\rangle$ proportional to the Slater $2p_\pi 2p_\pi$ overlap integral, the proportionality constant being evaluated at the equilibrium bond distance. The result gives a simple Hückel matrix which converts smoothly from a hexatriene to a butadiene-like molecule.

Rehybridization and bond energy. Dewar and Schmeising[9] have suggested that the energy of a bond alters with the hybridization of the atoms joined by that bond. Starting from a set of experimental bond lengths they developed an empirical relation between bond length and bond energy. Since there exists a reasonably good linear relation between bond length and the hybrid character of a bond, this provides a relation between hybridization and bond energy. Application of the method of Dewar and Schmeising to the hexatriene-cyclohexadiene reaction gives $\Delta H° = -19{\cdot}4$ kcal/mole. A comparison figure can be obtained from the measured equilibrium constant for the cyclooctatriene⇌bicyclo[4.2.0]octa-2,4-diene[10] ($K = 0{\cdot}176$ at 80°) reaction. In conjuction with the strain energy of 26·2 kcal/mole for cyclobutane,[11] of 8·9 for cyclooctatriene,[12,13] and of 4·8 for 1,3-cyclohexadiene,[12]* this gives an estimate of the $\Delta G°$ for hexatriene to cyclohexadiene of *ca* -21 kcal/mole. Since $\Delta S°$ for the ring closure is certainly negative, the value of $\Delta H°$ obtained from Dewar and Schmeising's data seems quite reasonable.

In view of the approximations involved in our calculations, and since we are only interested in the hybridization range from sp^3 to sp^2, we replaced the tratrix equation of Dewar and Schmeising by the linear equation

$$E(\text{kcal/mole}) = 377{\cdot}0 - 189{\cdot}4\,r$$

where r = bond length in Å.

From this we derive the equation below for the change in energy of a C—C single bond which results from the rehybridization (η). The equation

*Note that for these conjugated dienes the ring strain here includes delocalization energy as well as normal strain energy terms.

Table 1. Properties of hybrid bonds

Bond type	Bond integral	Bond length	Bond energy
sp^3–sp^3	$\langle(1/2S + \sqrt{3}/2P)\|H\|(1/2S + \sqrt{3}/2P)\rangle$	1·544 Å	84·56
sp^2–sp^2	$\langle(1/\sqrt{2}S + \sqrt{2}/3P)\|H\|(1/\sqrt{2}S + \sqrt{2}/3P)\rangle$	1·484 Å	95·99
sp–sp	$\langle(1/\sqrt{2}S + 1/\sqrt{2}P)\|H\|(1/\sqrt{2}S + 1/\sqrt{2}P)\rangle$	1·379 Å	119·75

was used to calculate the energy change for the C_1—C_2 and C_5—C_6 bonds during

$$\Delta E_{C-C} = 189{\cdot}4[1{\cdot}708 - 0{\cdot}656(0{\cdot}125 + \tfrac{1}{2}(3 + \eta^2))] - 287{\cdot}1$$

rehybridization. For C—H bonds a simpler equation was developed and applied to the four C—H bonds on C_1 and C_6.

$$\Delta E_{C-H} = 17{\cdot}54 - 52{\cdot}64\,(1/2 + \eta^2).$$

Strain energy. Generally three terms appear under this heading, bond angle strain, torsional strain and non-bonded interactions. For convenience we have used fixed 120° bond angles for all positions except those at the two terminal carbon atoms. Therefore, no attempt was made to introduce energy changes resulting from bond angle deviations. In view of the simple unhindered nature of the system, exclusion of bond angle strain seems unlikely to influence the conclusions in any significant way (see below). We have also chosen to neglect any terms due to torsional strain. There are two rotational processes occurring during the reaction. The rotation described by θ is very closely related to rotation about the central bond in butadiene. The confusion surrounding estimates of the magnitude of that rotational barrier has been surveyed.[13] A significant portion of this barrier must involve the loss of delocalization energy to the pi system. That portion is taken into account in our calculation of the pi system energy. In lieu of any reasonable estimate of the portion of the barrier not due to delocalization, we have chosen to neglect this factor. Rotations parameterized by ω have no experimental equivalents but since the major energy change is accounted for in our pi energy calculation, the remainder is closely related to the single bond rotation in propene. It should not exceed therefore the 1·98 kcal/mole value for propene,[14] and its neglect is obviously justifiable.

The non-bonded interaction energy is an important term to be considered. The two groups *cis* to the polyene chain at the terminal carbons will point toward the inside of the developing ring for values of $\theta > 90°$. In the disrotatory process in particular these groups point at one another until rehybridization and rotation move them toward their final positions outside the ring. Accordingly these interactions were accounted for using the potential function of Hendrickson, which has proved successful for treating conformations of medium rings, another case where non-bonded interactions play an important role. Since we have chosen not to take bond angle deviation into

$$V(H,H) = 10^{4-2r} - 49{\cdot}2/r^6$$

where r = H,H distance

account explicitly, we have used a relatively soft potential function for the non-bonded interactions. Clearly a large part of any interaction which appears between hydrogens on C_1 and C_6 could be most economically relieved by bending both C—H bonds. This cannot occur in the model with fixed bond angles, hence the soft potential function.

Calculations. A program was written which permitted calculation of the positions of all the atoms and orbitals and from these the relevant energy terms. Calculations were limited to conformations of the system which retain the symmetry element pertinent to the conservation of orbital symmetry theory.[2] A problem arises in regard to the pi system energy which comes out of the Hückel calculation in beta units. It is not possible to assign beta a precise equivalent in kcal/mole. For example beta could be evaluated by equating the 2·00 β of a pi bond to the activation energy of the *cis*-2-butene to *trans*-2-butene interconversion,[15] a process which gives β = 25 kcal/mole. Perhaps an equally appropriate evaluation could be made by equating the calculated delocalization energy for butadiene with the experimental value, which gives β = 6 kcal/mole. In view of this problem, values of beta from 5–25 kcal/mole in jumps of 2 kcal/mole were used to compute a series of total energies, and final decision was left to an inspection of the computed results.

RESULTS AND DISCUSSION

The most striking result of our calculations was the lack of a maximum in the plot of energy *vs* θ (Fig 2). This result is independent of the kcal equivalent assigned to beta. A second feature of the calculations is the minimum which appears at θ = 150° in the disrotatory path and θ = 162° in the conrotatory route. In part these are artifacts of the model, since the fixed bond angles and bond lengths ensure that the planar cyclohexadiene will be of higher energy than a non-planar form. However the depth of the depression is accentuated by the pi energy calculation which permits a large degree of delocalization over the six atom system to persist until planarity is established. While it is gratifying to find that the calculations predict a lower energy path for the disrotatory route in accord with the conservation of orbital symmetry theory, failure to predict a transition state is unfortunate for our interest in learning more about the geometry of the system at that point.

We think that the failure of the model to give an energy maximum rests in the calculation of the pi system energy. However the route to a cure is not obvious. Oosterhoff and Van der Lugt[16] carried out some refined calculations by a valence bond method for the electrocyclic reaction of butadiene and cyclobutene using a model whose geometric restrictions were similar to ours and found that the preferred conrotatory process had no energy maximum. We have adopted an expedient solution which built in an artificial maximum by reducing the

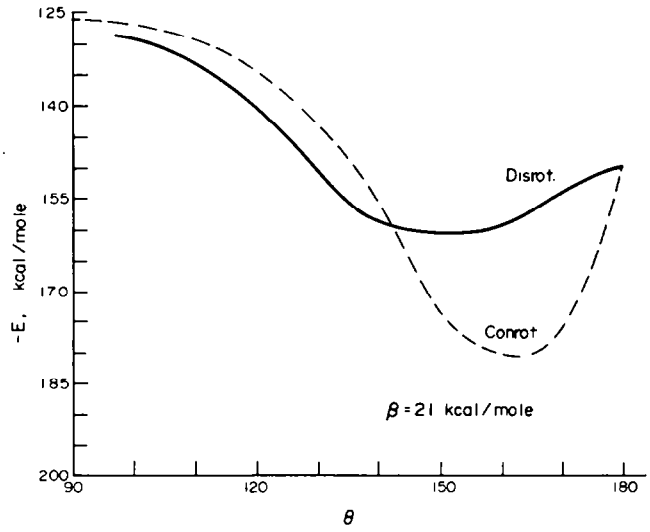


Fig. 2. Plot of calculated values for total potential energy *vs* the angle of rotation θ for Hückel β set equal to 21 kcal/mole.

kcal equivalent of beta and then raising it back to the original value. Since the kcal equivalent for beta is larger for an effectively isolated pi bond than for the delocalization energy this solution may be construed as assigning the pi system a greater extent of delocalization at the transition state than in the initial or final states.

It might appear at this point that the position of the maximum would become a plaything of the arbitrary variation of beta. Within some rather narrow limits this is indeed true, but a really capricous variation is not possible. If the beta value is decreased rapidly and increased again slowly so as to produce a maximum early in the reaction course, the C_1–C_6 distance in the transition state assumes absurdly large values. Reversal of this variation to obtain a late maximum produces curves with more than a single maximum. Thus the requirement of a physically reasonable solution places rather strict requirements on the nature of the transition state. While the height of the energy barrier can be varied arbitrarily, this can be calibrated against the experimental results. Thus it is possible to draw some conclusions about the nature of the transition states from this admittedly oversimplified approach. The most reasonable curves for a plot of energy *vs* θ are shown in Fig 3, and the relevant geometric details are given in Table 2 for

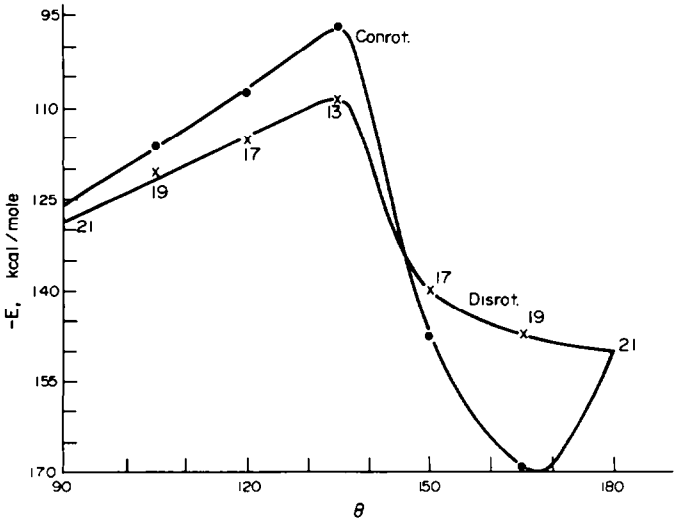
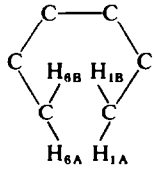


Fig. 3. Plot of calculated values for total potential energy *vs* the angle of rotation θ for variable values of Hückel β as indicated at points on the curves.

Table 2. Geometries of the calculated transition states

	C_1C_6	$H_{1A}H_{6A}$	$H_{1B}H_{6B}$	$H_{1A}H_{6B}$	$H_{6A}H_{1B}$
Disrotatory	2·0	2·8	1·6	3·1	3·1
Conrotatory	2·5	3·4	3·4	3·3	3·3

The hydrogen atoms are positioned as follows:



the two transition states. Also the magnitudes of the energy terms contributing to the transition state energies are listed in Table 3.

Table 3. Terms contributing to the transition state energies

Energy	Disrotatory	Conrotatory
Pi	76 (5·90 β)	83 (6·43 β)
Single bond	42	15
Rehybridization	− 6	− 0·5
Non-bonded interaction	− 4	0·0

The geometry for the disrotatory transition state is not completely acceptable but it is useful. Not unexpectedly the C_1—C_6 distance is overly long for the bond energy noted, but that results from the relatively slow decrease of the Slater overlap integral with distance. Similarly the absurdly short H_{1B}–H_{6B} internuclear distance results from the soft non-bonded interaction potential function used. This would be expected to achieve relief by C—H bond bending and a small increase in rehybridization. In view of the experimental estimates of the energy difference between the allowed and disallowed paths (*ca* 12–18 kcal/mole) recently published,[17] it is amusing that when the activation energy for the disrotatory calculation is set at *ca* 20 kcal/mole, the difference between the disrotatory and conrotatory routes is calculated at 12 kcal/mole. The only conclusion we wish to draw from this is that the energy difference between the two stereopaths is large enough to insure that steric hindrance (large *cis* at both C_1 and C_6) is more likely to induce alternative reactions than to force the conrotatory route to be adopted. This is in accord with the experimental data now extant. Thus, for example all *cis*-2,4,6-octatriene undergoes a 1,7-hydrogen shift[4] rather than electrocyclization.

A more interesting conclusion which might be drawn from the present calculation is that the single bond is well on the road to formation at the transition state, a process which largely disconnects carbons 1 and 6 from the conjugate system. Also the θ rotation has twisted the p-orbitals at C_2 and C_5 so that a dihedral angle of *ca.* 45° exists between those and the p-orbitals of C_3 and C_4. The latter pair retain a parallel alignment. In effect the transition state has a good pi bond between C_3 and C_4, a partial sigma bond between C_1 and C_6, but has left C_2 and C_5 partially isolated. The result suggests that the influence of substituents should vary markedly depending on the position of attachment, and the largest electronic effect should appear for substituents at C_2 and C_5. This point will be considered in detail in a companion article.

APPENDIX

Rehybridization of bonds at C_1 *and* C_6. Consider the left half of the hexatriene molecule for illustration. The auxiliary coordinate system at C_6 is shown in Fig 4. Rehybridization is introduced in this coordinate system in terms of η_1. Thus the three orbitals used by C_6 to form bonds to H_A, H_B and the p-orbital which will convert to the C_1—C_6 sigma bond will be those shown here.

$$\phi_{C_6H_A} = \frac{1}{\sqrt{3+\eta_1^2}}S + \frac{1}{\sqrt{(2+\eta_1^2)(3+\eta_1^2)}}P_{x'} - \frac{1}{\sqrt{2}}P_{y'} - \frac{\eta_1}{\sqrt{2(2+\eta_1^2)}}P_{z'}$$

$$\phi_{C_6H_B} = \frac{1}{\sqrt{3+\eta_1^2}}S + \frac{1}{\sqrt{(2+\eta_1^2)(3+\eta_1^2)}}P_{x'} + \frac{1}{\sqrt{2}}P_{y'} - \frac{\eta_1}{\sqrt{2(2+\eta_1^2)}}P_{z'}$$

$$\phi_{C_6C_1} = \frac{\eta_1}{\sqrt{3+\eta_1^2}}S + \frac{\eta_1}{\sqrt{(2+\eta_1^2)(3+\eta_1^2)}}P_{x'} + \frac{\sqrt{2}}{\sqrt{2+\eta_1^2}}P_{z'}$$

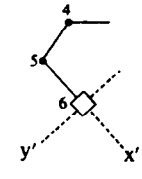


Fig 4. Auxiliary coordinate system at C_6.

The $P_{x'}$, $P_{y'}$ and $P_{z'}$ components of these were used to define a *unit* vector in each case. The x', y' and z' components of these vectors are listed in Table 4.

Table 4. Components of the unit vectors at C_6 in the auxiliary coordinate system

	x'	y'	z'
CH_A	$\frac{1}{2+\eta_1^2}$	$\sqrt{\frac{3+\eta_1^2}{2(2+\eta_1^2)}}$	$-\frac{\eta_1}{2+\eta_1^2}\sqrt{\frac{3+\eta_1^2}{2}}$
CH_B	$\frac{1}{2+\eta_1^2}$	$-\sqrt{\frac{3+\eta_1^2}{2(2+\eta_1^2)}}$	$-\frac{\eta_1}{2+\eta_1^2}\sqrt{\frac{3+\eta_1^2}{2}}$
Orb	$\frac{\eta}{\sqrt{3(2+\eta_1^2)}}$	0	$\sqrt{\frac{2(3+\eta_1^2)}{3(2+\eta_1^2)}}$

REFERENCES

[1]Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, *via* an International Award to E. N. Marvell for the academic year 1965–1966. The author is indebted to Professor E. Heilbronner for his kind hospitality and advice during the time this work was in progress

[2]R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry* Verlag Chemie, Weinheim, Germany (1970)

[3]E. Havinga and J. L. M. A. Schlattman, *Tetrahedron* **16**, 146 (1961), and earlier papers in the series

[4]D. S. Glass, J. W. H. Watthey and S. Winstein, *Tetrahedron Letters* 377 (1965); E. N. Marvell, G. Caple and B. Schatz, *Ibid.* 385 (1965); E. Vogel, W. Grimme and E. Dinné, *Ibid.* 391, (1965)

[5]E. N. Marvell, G. Caple, T. A. Gosink and G. Zimmer, *J. Am. Chem. Soc.* **88**, 619 (1966)

[6]E. N. Marvell, G. Caple and I. Shahidi, *Ibid.* **92**, 5641 (1970)

[7]A preliminary account of that work has been presented, E. N. Marvell, E. Heilbronner and H. Baumann, *Abstracts* 153rd *National Meeting of the American Chemical Society*, Miami, Fla., April (1967)

[8]J. B. Hendrickson, *J. Am. Chem. Soc.* **86**, 4854 (1964); **89**, 7047 (1967) and earlier papers in the series. For a similar calculation to that described here see also, M. Simonetta, G. Favini, C. Mariani, and P. Gramaccioni, *Ibid.* **90**, 1280 (1968)

[9]M. J. S. Dewar and H. S. Schmeising, *Tetrahedron* **11**, 96 (1960)

[10]A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, *J. Am. Chem. Soc.* **74**, 4867 (1952)

[11]S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.* **71**, 261 (1952)

[12]S. W. Benson, *Thermochemical Kinetics*, p. 179. Wiley, New York (1968)

[13]R. Hoffman, *Tetrahedron* **22**, 521 (1966)

[14]E. B. Wilson, Jr., *Advan. Chem. Phys.* **2**, 367 (1959)

[15]W. F. Anderson, J. A. Bell, J. M. Diamon and K. R. Wilson, *J. Am. Chem. Soc.* **80**, 2384 (1958)

[16]W. T. A. M. Van der Lugt and L. J. Oosterhoff, *Chem. Commun.* 1235 (1968)

[17]J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.* **90**, 1920 (1968); A. Dahmen and R. Huisgen, *Tetrahedron Letters* 1465 (1969); S. W. Staley and T. J. Henry, *J. Am. Chem. Soc.* **93**, 1292 (1971)