a greater degree of progress toward sp^2 geometry at the transition state, increasing the extent of interaction, particularly by resonance, between the reaction center and polar substituents.

Dehydration of the carbinolamine derived from 5-nitrofurfural and phenylhydrazine is markedly susceptible to base catalysis, while those derived from other furfurals exhibit very small contributions from this pathway. Thus the polar effects on the base-catalyzed pathway are the largest for this particular dehydration pathway as they are for dehydration of benzaldehyde phenylhydrazine carbinolamine.[4] As above, this behavior must reflect the importance of electron withdrawal in the formation of the double bond in the product.

Registry No.—Phenylhydrazone, 100-63-0; 5-bromofurfural phenylhydrazone, 34220-06-9; 5-methylfurfural, 620-02-0; furfural, 98-01-1; 5-bromofurfural, 1899-24-7; 5-nitrofurfural, 698-63-5.

Acknowledgment.—The author is indebted to Dr. Eugene H. Cordes for helpful comments concerning this work.

The Influence of Configuration on Transmission of Electronic Effects in α,β-Unsaturated Ketones

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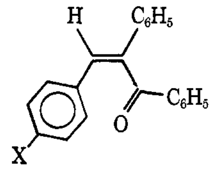
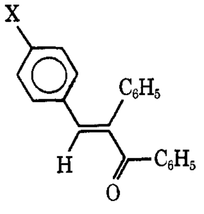
A series of zusamen (Z)- and entgegen (E)-α-phenylchalcones (1,2-diphenyl-3-arylpropenones) have been prepared and configurational assignments have been made to them. Their carbonyl stretching frequencies have been measured in carbon tetrachloride solutions. A good linear free-energy relationship was obtained between ν(C=O) and σ^+ for the E isomers ($r = 0.980$). On the other hand, the Z isomers gave only a poor correlation ($r = 0.798$). An unprecedentedly large ρ_E/ρ_Z ratio of ~6 was observed. The ρ value for the Z isomers suggests that this system is essentially insensitive to substituent effects. The data were also treated using the Swain–Lupton approach. Comparisons of the linear free-energy results obtained from the α-phenylchalcone system are made with other analogous systems.

The alteration of transmission of electronic effects through an intervening link by changing the geometric relationship between substituent and reaction site has been noted in several systems.[2] In aliphatic systems a change from E to Z isomers resulted in an increase in sensitivity to substituents as judged by the magnitudes of the Hammett ρ values and this observation has been attributed to field effects. In aryl systems a reduction in sensitivity to substituents with the same configurational change has been noted. In spite of growing interest and an increasing number of reports on linear free-energy relationships of α,β-unsaturated ketone systems,[3,4] the effect of geometric alterations on substituent effect transmission in such systems does not appear to have been reported. To attempt to assess this effect and as a continuation of a general investigation[4] of linear free-energy relationships of α,β-unsaturated ketones, we have measured the carbonyl stretching frequencies [ν(C=O)] of a series of (Z)- and (E)-α-phenylchalcones [1,2-diphenyl-3-(para-substituted phenyl)propenones] (I and II).



I



II

α-Phenylchalcones.—The α-phenylchalcones were prepared using the approach previously described by Stobbe[5] which usually resulted in a mixture of (Z)- and (E)-α-phenylchalcones. Frequently, the reaction sequence gave mainly the E isomer, and consequently to acquire adequate amounts of the Z isomer the E isomer was subjected to photoequilibration type conditions and the resulting mixtures were separated by column chromatography.

The configurations of the isomers were assigned on the basis of the extinction coefficient of their uv absorption maximum in analogy with the assignments made for **5**, **13**, **8**, and **16** by Lutz and Black.[6] The series of compounds assigned the E configuration consistently, with the exception of **16** as previously noted,[6] exhibited absorption maxima at wavelengths longer than the Z isomers. The series assigned the Z configuration exhibited ν(C=O) bands which were at higher frequencies, generally about 10 cm^{-1}, than the corresponding E isomers (see Table I). This is in accord with the idea that the steric interaction of the 3-aryl group with the benzoyl group in the Z isomer results in the deconjugation of the carbonyl and styryl groups and hence a shift of ν(C=O) to higher frequency. The configurational assignments[6] to the parent members of this series made by consideration of uv absorptions have now been independently confirmed by ir measurements.

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[1] American Chemical Society Petroleum Research Fund Scholar.

[2] (a) K. Bowden and D. C. Parkin, *Can. J. Chem.*, **46**, 3909 (1968); (b) R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **31**, 3423 (1966); (c) M. Charton, *ibid.*, **30**, 974 (1965); (d) A. B. Turner, R. E. Lutz, N. S. McFarlane, and D. W. Boykin, Jr., *ibid.*, **36**, 1107 (1971); (e) J. J. Bloomfield and R. Fuchs, *ibid.*, **26**, 2991 (1961); (f) R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *ibid.*, **27**, 733 (1962).

[3] (a) J. R. Dimmock, P. L. Carter, and P. D. Ralph, *J. Chem. Soc. B*, 698 (1968); (b) S. Toma and A. Perjessy, *Chem. Zvesti*, **23**, 343 (1969); (c) A. Perjessy, *ibid.*, **23**, 905 (1969).

[4] (a) N. L. Silver and D. W. Boykin, Jr., *J. Org. Chem.*, **35**, 759 (1970); (b) M. L. Ash, F. L. O'Brien, and D. W. Boykin, Jr., *ibid.*, **37**, 106 (1972); (c) W. F. Winecoff, III, and D. W. Boykin, Jr., *ibid.*, **37**, 674 (1972); (d) R. W. Woodard and D. W. Boykin, Jr., *Chem. Commun.*, 628 (1970).

[5] H. Stobbe and F. J. Wilson, *Ann.*, **374**, 237 (1910).

[6] W. B. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, **75**, 5990 (1953).

TABLE I

α-PHENYLCHALCONES

Z isomers			E isomers		
Compd	X	ν(C=O), cm^{-1}	Compd	X	ν(C=O), cm^{-1}
1	p-CH$_3$O	1670.6	**9**	p-CH$_3$O	1657.7
2	p-CH$_3$	1671.4	**10**	p-CH$_3$	1660.1
3	p-C$_6$H$_5$	1671.6	**11**	p-C$_6$H$_5$	1660.7
4	p-F	1670.7	**12**	p-F	1661.5
5	p-H	1671.1	**13**	p-H	1660.8
6	p-Cl	1672.0	**14**	p-Cl	1662.6
7	p-Br	1671.6	**15**	p-Br	1663.2
8	p-NO$_2$	1672.4	**16**	p-NO$_2$	1667.6

Linear Free-Energy Relationships.—The values for ν(C=O) for eight geometric pairs of α-phenylchalcones measured in carbon tetrachloride solution are listed in Table I. The difference in ν(C=O) for the p-methoxy- (**9**) and the p-nitro- (**16**) (E)-α-phenylchalcones, $\sim$10 cm^{-1}, provides an ample spread in σ values for developing a significant linear free-energy relationship. On the other hand the analogous difference in the Z series is only $\sim$2 cm^{-1}. In view of the error in measurement of ν(C=O) interpretation of correlations derived from the Z series should be viewed with some skepticism.

Both configurational isomers show shoulders on the carbonyl band. The shoulders presumedly arise from conformational bands. It is assumed that lack of assignment of these bands is of no particular consequence to this study, since it has been shown that effectiveness of transmission does not vary over a range of about 30% for conformational isomers in several other α,β-unsaturated ketone systems.[4c]

The stretching frequencies of both isomeric series have been correlated with σ^+ values taken from reported tabulations.[7] Figure 1 contains a graphical presentation and Table II contains the results of statistical treatment[8] for both series. A good correlation is observed for the E series (r = 0.980), whereas a poor correlation is obtained with the Z system (r = 0.798).

TABLE II

RESULTS OF STATISTICAL TREATMENT USING σ^+ CONSTANTS[a,b]

System	n	ρ	s	i	c
(Z)-Chalcone	8	1.10	0.40	1671.5	0.798
(E)-Chalcone	8	6.35	0.62	1662.0	0.980
(E)-APCA[c]	7	7.07	2.64	1674.0	0.826

[a] See ref 4a and 8. [b] n, number of points; ρ, slope as determined by method of least squares; s, standard deviation; c, correlation coefficient; i, intercept. [c] Data taken from ref 9; values used for p-CH$_3$O, p-CH$_3$, p-H, m-CH$_3$O, p-Cl, m-Cl, and p-NO$_2$ substituents. See also footnote 10.

Comparison of the ρ value (6.35) obtained from the E series with the value (5.36) obtained from five similarly substituted chalcones[4a] shows that there is little change in the effectiveness of the transmission of electronic effects by the addition of the α-phenyl group to the (E)-chalcone system. This suggests that a serious steric effect on the chalcone system is not introduced by the addition of a large group and that the inductive effect of the α-phenyl is not detrimental to transmission. The implication is that the β-phenyl and the benzoyl group remain essentially coplaner. This conclusion is in accord with ones previously drawn from uv studies.[6]

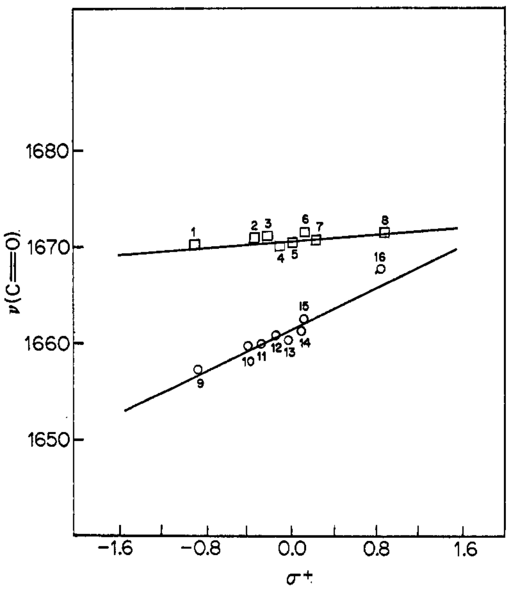

Figure 1.—Plot of ν(C=O) *vs.* σ^+: □, Z isomers; ○, E isomers.

An investigation of the effect of substituents on the carbonyl stretching frequency of substituted α-phenylcinnamic acids (APCA), measured in the solid state, has been reported.[9,10] Table II contains the results of least-squares treatment of the (E)-APCA data. The correlation is poor; nevertheless, the ρ value is approximately that which we note for the (E)-α-phenylchalcones.[10]

The ρ value for the (Z)-α-phenylchalcone series is dramatically different from the E value even bearing in mind the error in measurement for the Z series. Essentially, the Z series is insensitive to substituent effects. This profound difference between geometric isomers is unprecedented. Previous studies of the effect of geometry on transmission of electronic effects in aryl systems have shown, by comparing $\rho_E:\rho_Z$ ratios, that the Z isomers generally transmit electronic effects from $\sim$50% as effectively to equally as well as the corresponding E isomers.[2] Table III contains a comparison of $\rho_E:\rho_Z$ for several sets of closely related geometric pairs. The $\rho_E:\rho_Z$ value reported here for the α-phenylchalcones is greater than those shown in the table by a

TABLE III

ρ-VALUE COMPARISON FOR Z AND E ISOMERS

System	Reaction	$\rho_E:\rho_Z$	Ref
α-Phenylchalcones	ν(C=O)	5.8	This work
α-Phenylcinnamic acids	Ionization	1.2	2a
α-Phenylcinnamic acids	Esterification	1.9	2a
Cinnamic acids	Ionization	1.4	2e
Cinnamic esters	Saponification	1.1	2e
Phenylbenzoylaziridines	Nmr chemical shifts	1.4	2d
Phenylcyclopropanecarboxylic acids	Ionization	1.1	2f
Phenylcyclopropanecarboxylic esters	Saponification	0.8	2f

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(7) C. D. Ritchie and W. F. Sager in "Progress in Physical Organic Chemistry," Vol. 2, Interscience, New York, N. Y., 1964.

(8) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(9) C. W. Bird and E. M. Briggs, *Spectrochim. Acta*, **25A**, 899 (1969).

(10) Data for only four Z isomers were reported and interestingly the ν(C=O) value for the p-NO$_2$ compound was at some 5-cm^{-1} lower frequency than that of the p-CH$_3$O analog. Therefore, we have not treated the reported data for this Z series by our statistical approach.

TABLE IV

RESULTS OF STATISTICAL TREATMENT USING F AND R CONSTANTS[a]

System	n	f	r	i	E	C	% R
(Z)-Chalcone	8	0.528 ± 0.346	2.30 ± 0.72	1671.5	0.374	0.858	64 ± 17
(E)-Chalcone	8	4.63 ± 0.430	9.66 ± 0.890	1661.1	0.465	0.991	46 ± 3
(E)-APCA[b]	7	6.56 ± 1.86	9.76 ± 3.15	1673.1	1.80	0.939	46 ± 11
(Z)-APCA[c]	5	−0.423 ± 0.044	−0.526 ± 0.088	5.61	0.041	0.994	35 ± 5
(E)-APCA[c]	5	−0.444 ± 0.122	−0.857 ± 0.244	6.92	0.113	0.974	46 ± 10
(Z)-APCA[d]	5	0.180 ± 0.020	0.191 ± 0.040	0.980	0.019	0.993	32 ± 5
(E)-APCA[d]	5	0.301 ± 0.042	0.494 ± 0.084	0.02	0.039	0.992	42 ± 5

[a] Swain–Lupton field and resonance parameters; see ref 11. These correlations were made using a multiple linear regression program written using the statistical analysis described in ref 11. Calculations were carried out on an IBM 7094 computer. % R values were calculated by the approach used in ref 4a. n, number of points; f, regression coefficient for field parameter; r, regression coefficient for resonance parameter; i, intercept; E, standard error of estimate; C, multiple correlation coefficient; % R defined in ref 4a. [b] The stretching frequency data for α-phenylcinnamic acids in the solid state have been reported.[9] The E isomers used in this correlation were those listed in Table II, footnote c. See also ref 10. [c] Correlation of pK data is reported for α-phenylcinnamic acids in ref 2a. Substituents used were p-H, p-CH$_3$O, p-CH$_3$, p-Cl, and p-NO$_2$. [d] Correlation of rate constants for esterification of α-phenylcinnamic acids with diphenyldiazomethane is reported in ref 2a. The substituents were the ones listed in c above.

factor of at least 3. The large difference may be the result of a greater degree of steric interactions in the more sterically complicated α-phenylchalcones in comparison with other less substituted systems. On the other hand, this difference may reflect the fact that most of the $\rho_E:\rho_Z$ ratios in Table III are derived from reaction data where developing charges make more extensive demands upon the substituents and thereby force a greater degree of coplanarity between the Z groups in question. To test this point, other geometric pairs should be investigated by methods which assess ground-state substituent effects.

Swain and Lupton[11] have developed a method which evaluates the significance of the resonance and field effect contributions to a two parameter linear free-energy relationship. The results of the treatment of the data for the (Z)- and (E)-α-phenylchalcones by this approach are listed in Table IV. Included for comparison with the α-phenylchalcone data in Table IV are the results from treatment of ir and reaction data previously reported on the APCA system.[2a,9,10]

It was noted (*vide supra*) that the Hammett ρ value for II was significantly greater than the value for I. If % R values are a measure of the transmission of resonance effects it can be seen from Table IV that there is no significant effect on transmission by resonance with changes in the geometric relationships of the molecule. The correlation for I is poor and consequently makes this observation tenuous at best for this system. On the other hand, the reactivity data listed in Table IV, for which good correlations are obtained, show little, if any, difference between the contribution of resonance to the correlation for the (Z)- and (E)-α-phenylcinnamic acids. Whether these results should be interpreted as evidence for the invalidity of the Swain–Lupton approach or as evidence which requires the rejection of the idea that diminution of transmission of electronic effects in the Z series is a result of deconjugation of the substituent and the reaction site remains to be tested by an independent approach.

TABLE V

α-PHENYLCHALCONES[a]

Compd	Mp (lit. mp), °C	λ, nm (ε × 10^{-3})	λ, nm (ε × 10^{-3})
		Z Isomers	
1	113–114 (113)[b]	257 (25.7)	294 (28.8)
2	91–92	260 (24.3)	286 (26.1)
3	163–164.5	260 (20.1)	306 (34.2)
4	115–117.5	259 (23.4)	279 (21.1)
5	85–87 (88–89)[c]	260 (20.3)	282 (19.4)
6	101–102	260 (29.8)	285 (30.6)
7	95–97	261 (26.6)	287 (28.2)
8	167–168 (168–168.5)[c]	251 (21.6)	328 (20.4)
		E Isomers	
9	84–85 (85)[b]	252 (17.4)	315 (18.9)
10	94–94.5	252 (15.4)	312 (16.9)
11	184–186	253 (20.3)	325 (26.3)
12	107–110	254 (16.4)	303 (14.4)
13	99–101 (103–103.5)[c]	250 (17.1)	299 (15.1)
14	98–100	255 (17.0)	304 (16.5)
15	96–98	255 (16.2)	305 (15.9)
16	155–157 (153–153.5)[c]	257 (16.3)	318 (16.4)

[a] All compounds except **5**, **8**, **13** and **16** were analyzed for C and H and all results were within ±0.3 of theory. [b] These isomers have been previously reported [A. Klages and F. Tetzner, *Ber.*, **35**, 3965 (1902)]; however, configurational assignments were not made. [c] Configurational assignments were made in ref 6.

Experimental Section

Infrared Frequencies.—The ir stretching frequencies for all of the α-phenylchalcones were determined using a Beckman IR-12 grating spectrometer in the expanded scale mode at scan rates of 8 cm^{-1} min, chart speeds of 1 in./min, and period setting of 8 (see ref 4a for comments on error). The spectra were taken on ~5% solutions of the compounds in spectral grade carbon tetrachloride at 35 ± 4° in a matched set of KBr cells of path length 0.05 mm. A weak band appeared at 1652 cm^{-1} in the spectra of all of the α-phenylchalcones, both E and Z isomers. The height of each band was measured as the distance from the maximum absorption of the 1652-cm^{-1} band to the point of maximum absorption of the carbonyl band. The frequencies were taken as the point at 25% of the height at half-band width and this value was determined by measurement from said point to a premarked wavenumber. The values shown in Table II are the average of six different scans taken on two separate days all of which gave frequencies which were within 0.3 cm^{-1} of one another. The carbonyl band of **1** was atypically complex; its band width was approximately twice as broad as the other E isomers. The band width used for determining ν(C=O) for **1** was obtained by superimposition of the spectrum of **2** on that of **1** and graphically plotting in the band shape. The ν(C=O) values deduced for **1** by other procedures resulted in values which deviated significantly from the Hammett line.

α-Phenylchalcones.—The approach used to prepare the α-phenylchalcones is similar to that described by Stobbe.[5] Anhydrous HCl was passed through a molten mixture of 0.05 mol of deoxybenzoin and 0.1 mol of substituted benzaldehyde for 4 hr. The resulting solid 3-chloro-3-aryl-1,2-diphenylpropanone was

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(11) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

washed with small quantities of cold ethanol followed by small quantities of ether. The crude chloropropanones, usually ~10 g, were used directly without further purification. Crude chloropropanone was dissolved in 250 ml of ethanol containing 0.3 mol of piperidine and refluxed for 24 hr. The solvent was evaporated under reduced pressure and the resulting residue was taken up in ether and washed with 5% HCl and with H_2O, dried ($CaSO_4$), and evaporated. The crude residue was placed on a chromatograph column packed with Al_2O_3. The eluent was typically benzene–low boiling petroleum ether mixtures.[12] The *Z* isomers were the first isomers to be eluted. Frequently, to obtain reasonable quantities of the *Z* isomers, benzene solutions of $\sim 10^{-3}$ *M E* isomers were irradiated for 24 hr with a 320-W uv lamp fitted with a 2537-A light source. The product of the irradiation was chromatographed as described above. The physical properties of the α-phenylchalcones prepared in this way are listed in Table V.

Table V contains melting points obtained with a Thomas-Hoover Uni-Melt and they are corrected. Also, Table V contains uv data obtained for the α-phenylchalcones in $\sim 10^{-5}$ *M* absolute ethanol solutions on a Beckman DK-2 spectrometer. Analyses were obtained by Atlantic Microlab, Atlanta, Ga.

Registry No.—**1**, 34236-57-2; **2**, 34236-58-3; **3**, 34236-59-4; **4**, 34236-60-7; **5**, 7512-67-6; **6**, 34236-62-9; **7**, 34236-63-0; **8**, 34236-64-1; **9**, 34236-65-2; **10**, 34236-66-3; **11**, 34236-67-4; **12**, 34236-68-5; **13**, 7474-65-9; **14**, 34236-70-9; **15**, 34236-71-0; **16**, 34236-72-1.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We wish to thank Professor R. E. Lutz for samples of **8** and **16**.

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[12] *Cf.* L. E. Friedrich and R. A. Cormier, *J. Org. Chem.*, **35**, 450 (1970).

Notes

The Rearrangement of 11,11-Dibromotricyclo[4.4.1.$0^{1,6}$]undecane

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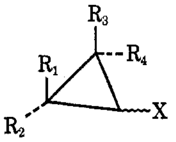
The solvolysis of various monocyclic and bicyclic cyclopropyl compounds has received widespread attention by numerous investigators during the past several years.[1] The impetus for this interest arises, for the most part, from the elegant and far-reaching theories of Woodward, Hoffmann, and DePuy concerning the electrocyclic reactions of cyclopropyl systems.[2] Product as well as kinetic studies have unequivocally demonstrated that in secondary, monocyclic systems (*e.g.*, **1**) electrocyclic opening during solvolysis proceeds in a concerted disrotatory fashion with the alkyl substituents trans to the leaving group rotating outward and those cis to the leaving group rotating inward.[1,3] These experimental findings are in complete agreement with theory.[2] In the bicyclic endo system **2**, again, experiment verifies theory. That is, solvolysis proceeds in a disrotatory fashion affording a cis-allyl cation, which is subsequently quenched by solvent. In the corresponding exo series **3**, experiment seems to support the intermediary of a "partially opened" cyclopropyl cation **4** which leads to cyclopropyl, cis-allyl, or trans-allyl products (or products derived from trans-allyl derivatives) when $n \leq 5$. The relative yields of these products depend on the magnitude of *n* and the reaction conditions. For those cases in which $n > 5$ only monocyclic allyl products are obtained, since the ring structure is now large enough to accommodate a transition state approaching that of the monocyclic series.[1,4-7]



1

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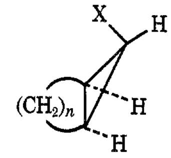

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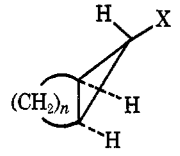

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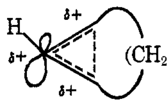
X = halogen, -OTs, -OTf



4

Substitution of a group which can stabilize a positive charge at the site of the leaving group (*e.g.*, c-Pr or Ph) results primarily in formation of cyclopropyl prod-

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[1] (a) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **94**, 125 (1972), and references contained therein; (b) T. M. Su, Ph.D. Thesis, Princeton University, 1970; (c) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 133 (1972).

[2] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

[3] P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

[4] G. H. Whitham and M. Wright, *Chem. Commun.*, 294 (1967).

[5] U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. M. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967).

[6] D. T. Clark and G. Smale, *J. Chem. Soc.*, 1050 (1969).

[7] D. Schober, Ph.D. Thesis, University of Chicago, 1969.