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Conformational Preferences in Acyclic Chloro Sulfides. A Semiquantitative Approach

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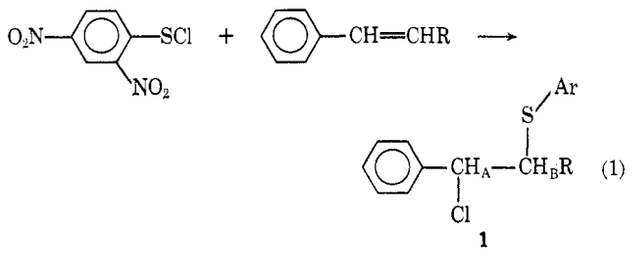
The erythro isomers in alkyl-substituted 1-chloro-1-phenyl-2-ethyl 2,4-dinitrophenyl sulfides increasingly favor the conformer having trans hydrogens as the size of R increases. The rates of solvolysis in 95% ethanol show evidence of anchimeric assistance by sulfur and give products of retained configuration. The rates are correlated with Taft's E_S values and corrected E_S values are taken. These E_S values are correlated with the nmr chemical shift of the 2′ hydrogen in the dinitrophenyl ring, and the E_S values are adjusted again. A linear free-energy correlation is made between the corrected E_S values and the equilibrium constant (gauche → trans conformers) $(J_{obsd} - J_G)/(J_T - J_{obsd})$. Unique values of the limiting coupling constants J_T and J_G cannot be obtained by this procedure. Reasons are given for choosing one solution of the correlation procedure, J_T = 13.5 Hz and J_G = 2.5 ± 1 Hz. The percentage of the trans conformer in several compounds is roughly calculated. The conformations of the solvolysis products (sulfide ethers and sulfide alcohols) are briefly discussed.

Previous work on acyclic conformational preferences has led to significant generalizations,[1,2] but, in general, one is still not able to predict conformation from a simple chemical formula. Each new type of group studied seems to introduce variables not previously suspected. The present work was intended to elucidate the effect of variation of the size of R on the conformational preferences of certain chloro sulfides of general structure **1**. A much larger variety of R groups was possible because of the facile synthesis indicated in eq 1.[3]



Part of our interest in these chloro sulfides stemmed from the possibility of an attractive interaction between these groups.[4] However, other work on alkyl-substituted chloro sulfides indicated that this interaction was weakly repulsive.[5] Since the conformation of each compound is the result of a balance between all attractive and all repulsive factors, which often are sensitive to exact internuclear distances, the study of the purturbation caused by moving from alkyl chloro sulfides to aryl chloro sulfides seemed attractive. In addition to the interaction between heteroatoms,[6] other factors, such as chlorine–alkyl and chlorine–hydrogen gauche interactions (presumably weakly attractive),[7] as well as the effects of restriction of motion of the SAr group, must be considered.[5]

Qualitative conformational preferences are determined from vicinal nmr coupling constants (J_{AB}). Large values for J_{AB} (10–13 Hz) indicate a preference for a conformer having trans hydrogens. Small values (1–3 Hz) show a preference for one of the conformers having gauche hydrogens. Intermediate values result from weighted means of the above values.[8] The nmr data for 12 pairs of diastereomers are listed in Table I. These data will be discussed in terms of the conformers shown in Chart I.

(1) D. H. R. Barton, *Experientia*, **23**, 316 (1950).
(2) (a) J. L. Mateos and D. J. Cram, *J. Amer. Chem. Soc.*, **81**, 2756 (1959); (b) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965, pp 331–343.
(3) (a) N. Kharasch, *J. Chem. Educ.*, **33**, 585 (1956); (b) G. H. Schmid and V. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966); (c) G. H. Schmid, *ibid.*, **46**, 3757 (1968); (d) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968); (e) F. T. Bond, *ibid.*, **90**, 5326 (1968); (f) H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956); (g) S. J. Cristol, R. Arganbright, G. Brindell, and R. M. Heitz, *ibid.*, **79**, 6035 (1957); (h) C. Brown and D. R. Hogg, *J. Chem. Soc. B*, 1262 (1968); (i) T. L. Jacobs and R. Macomber, *J. Org. Chem.*, **33**, 2988 (1968); (j) G. Beverly, D. R. Hogg, and J. H. Smith, *Chem. Ind. (London)*, 1403 (1968).
(4) T. Bjorvatten and O. Hassel, *Acta Chem. Scand.*, **15**, 1429 (1961).
(5) G. M. Underwood and C. Kingsbury, *J. Org. Chem.*, **38**, 1553 (1973).
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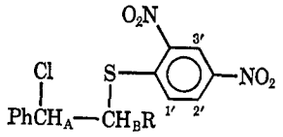
(7) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954, p 15.
(8) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

TABLE I

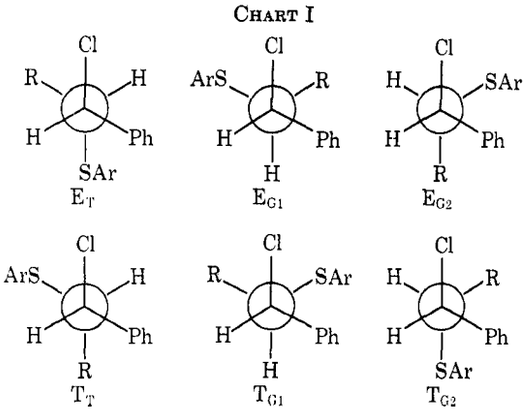
60-MHz CHEMICAL SHIFTS AND COUPLING CONSTANTS OF 2-12



Compd 2	R	Mp, °C	J, Hz J_{AB} ($CDCl_3$)[b,e]	J_{AB} (DMSO)[c]	J_{BR} ($CDCl_3$)[e]	Chemical shifts ($CDCl_3$)[b] A[e]	B[e]	1′	2′	3′
	H	148	6.2, 8.5			5.12	3.74	7.55	8.31[a]	9.02
erythro-3	CH_3	92	7.1	7.1		5.03	3.99	7.52	8.20[a]	8.79[a]
threo-3		94	5.7	6.5		5.11	4.12	7.51	8.21	8.67
erythro-4	C_2H_5	144	8.7	8.7		4.96	3.82	7.55	8.12[a]	8.65[a]
threo-4		127	4.8	5.9		5.27	3.87	~7.4	8.21	8.91
erythro-5	*i*-C_3H_7	162	10.7	11.0	2.4	4.93	3.78	7.44	8.04[a]	8.42[a]
threo-5		138	6.1	7.6	6.2	5.32	3.77	~7.4	8.10	8.55
erythro-6	*t*-C_4H_9	134	4.7			5.46	3.88	7.86	8.21	8.69
threo-6		143	1.6			5.62	3.41	6.50	7.70	8.54
erythro-7	$CH(C_2H_5)_2$	161	11.0		2.8	5.12	3.74	7.55	8.01[a]	8.47
threo-7		116	7.0		~4	5.35	4.02	7.61	8.21	8.82
erythro-8	$CH_2C(CH_3)_3$	116	7.2		1.2, 8.7	4.90	3.81	7.65	8.19[a]	8.69[a]
threo-8		153	4.3		2.2, 8.3	5.21	3.94	~7.5	8.21	8.98
erythro-9	C_3H_5[f]	147	6.4		8.5	5.18	3.41	7.62	8.21[a]	8.78[a]
threo-9	C_3H_5	142	5.1		9.4	4.94	3.72	~7.4	8.19	8.92
erythro-10	C_4H_7[f]	105	7.0		8.4	5.05	3.95	7.74	8.19[a]	8.72
threo-10	C_4H_7	105	3.7		9.5	5.22	3.78	7.06	8.01	8.82
erythro[d]-10′	C_4H_7[f]	112	5.4		~8.4	4.76	4.24	~7.4	8.15	8.96
threo[d]-10′	C_4H_7	125	4.5		~9.2	5.00	3.84	7.98	8.26	8.82
erythro-11	C_5H_9[f]	148	9.5		~4.4	5.00	4.01	7.58	8.10[a]	8.55[a]
threo-11	C_5H_9	109	4.2	5.2	~7.5	5.35	3.75	~7.07	7.95	8.74
erythro-12	C_6H_{11}[f]	174	10.8		~2.9	4.99	3.72	7.42	8.03[a]	8.47[a]
threo-12	C_6H_{11}	139	5.4	6.8	~5.4	5.40	3.65	~7.3	8.04	8.77

[a] Determined at 100 MHz, 1.0% w/v in $CDCl_3$, corrected to 60 MHz. [b] *Ca.* 10% w/v solution, at 60 MHz. [c] 5.0% w/v solutions. [d] The chloride and sulfide groups in **10** are reversed in **10′**. [e] The coupling constants and chemical shifts were verified by computer simulation. Parameters were varied until the plot of the simulation was superimposible on the original spectrum. [f] Cycloalkyl groups.

CHART I



With increasing size of R (up to *tert*-butyl), the erythro isomers show a monotonic increase in J_{AB}, indicative of a growing preference for E_T (Chart I). This behavior is common to the majority of systems studied to date.[9,10a] The now familiar discontinuity occurs in moving from R = isopropyl (**5**) to R = *tert*-butyl (**6**).[10] This change gives rise to an apparent preference for a conformer having gauche hydrogens. However, the variation of dihedral angles from near 60° in order to achieve a more comfortable arrangement of groups in E_T would serve to reduce J_{AB}. The coupling constant may also be affected by the spreading of the C–C–*tert*-butyl bond angle.[10d] However, the lack of mutual shielding of the aromatic groups (*vide infra*) is consistent with a much smaller population of E_T in **6** than in **5**.

Compound **8** (R = neopentyl) shows an apparent preference for E_T of about the same magnitude as that in **3** (R = methyl), which was unexpected on the basis of relative sizes of R. However, as Chart II shows, the coupling constants of the methylene hydrogens are abnormally small. Again, bond angle spreading may be in effect, thus reducing the effect size of the neopentyl group.

The effect of size is strikingly evident in the erythro cycloalkyl compounds **9–12**. The cyclopropyl and cyclobutyl groups have apparent conformational preferences of about the same order as methyl. Where R = cyclohexyl, the preference for E_T is slightly larger than that of its closest analog, isopropyl. The compression of bond angles necessary for the closing of the small rings results in widening of the exocyclic bond angles,[11]

(9) One must be careful how the erythro diastereomer is defined. Strictly speaking, the above observation holds true where erythro configuration is defined on the basis of size [H. E. Zimmerman and W. Chang, *J. Amer. Chem. Soc.*, **81**, 3634 (1959)], and preferably where attractive interactions are absent.

(10) (a) C. Kingsbury and D. Best, *J. Org. Chem.*, **32**, 6 (1967); (b) H. Bodot, J. Fediere, G. Pouzard, and L. Pujol, *Bull. Soc. Chim. Fr.*, 3260 (1968); (c) L. M. Jackman, and D. Kelly, *J. Chem. Soc. B*, 110 (1970); (d) C. Altona and D. Faber, *Chem. Commun.*, 1210 (1971).

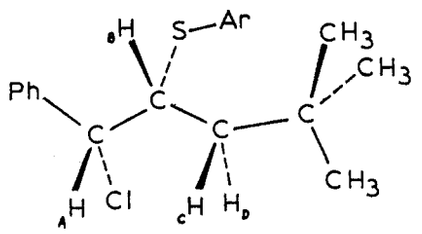
(11) H. C. Brown and M. Gerstein, *J. Amer. Chem. Soc.*, **72**, 2826 (1950).

TABLE II

RATES OF SOLVOLYSIS AND ACTIVATION PARAMETERS OF 2-12 IN 95% ETHANOL

Compd	R	$k_{obsd} \times 10^4$, sec^{-1} 50.0°	60.0°	70.0°	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
2	H	0.0278 ± 0.0001		0.47 ± 0.02		
erythro-3	CH_3	0.916 ± 0.014	2.27 ± 0.01	5.37 ± 0.06	18.9	−18.8
threo-3		0.036 ± 0.001	0.082 ± 0.0003	0.21 ± 0.01		
erythro-4	C_2H_5	2.61 ± 0.01	6.15 ± 0.15	14.1 ± 0.1	17.9	−19.6
threo-4		0.042 ± 0.001	0.11 ± 0.01	0.26 ± 0.01		
erythro-5	*i*-C_3H_7	5.30 ± 0.08				
threo-5		0.025 ± 0.007	0.062 ± 0.001	0.17 ± 0.01		
erythro-6	*t*-C_4H_9	124 ± 1			15.1	−20.6
threo-6		0.012 ± 0.01	0.028 ± 0.01	0.096 ± 0.001		
erythro-7	$CH(C_2H_5)_2$	3.67 ± 0.04				
threo-7				0.20 ± 0.01		
erythro-8	$CH_2C(CH_3)_3$	3.13 ± 0.01				
threo-8		0.034 ± 0.02	0.095 ± 0.002	0.23 ± 0.04		
erythro-9	C_3H_5	1.22 ± 0.01				
threo-9				0.17 ± 0.01		
erythro-10	C_4H_7	1.21 ± 0.01				
threo-10				0.31 ± 0.01		
erythro-11	C_5H_9	4.99 ± 0.05				
threo-11				0.55 ± 0.02		
erythro-12	C_6H_{11}	6.50 ± 0.05	16.7 ± 0.2	35.8 ± 0.3	18.3	−16.5
threo-12		0.045 ± 0.002	0.11 ± 0.01	0.33 ± 01		

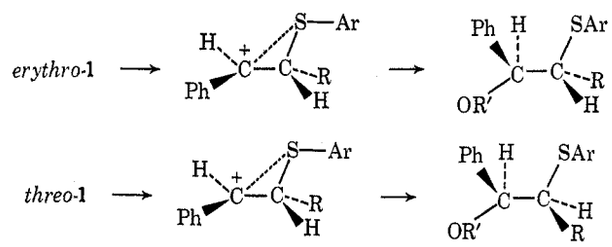
CHART II



a

J_{AB} = 7.2 Hz; J_{BC} = 1.2 Hz; J_{BD} = 8.7 Hz

CHART III



and leads to a reduction of the steric interaction with the neighboring phenyl or chloro group.

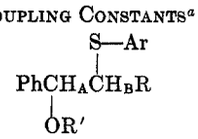
The regular increase in J_{AB} with increasing size of R prompted an attempt to establish a linear free energy correlation between the nmr data and the rates of solvolysis of these chlorides. As Table II shows, the rate of solvolysis of the erythro isomers increases as the size of R increases. It is quite reasonable that the same factors that affect conformation should also affect the rate of reaction. These solvolyses are subject to anchimeric assistance of ionization by neighboring sulfide.[12] Thus, the erythro isomers, which form the quite stable trans episulfonium ion (Chart III), are more reactive than the threo isomers, which form the less stable cis episulfonium ion. The trends of change of the nmr parameters of the solvolysis products as R is varied are consistent with products formed with retention of configuration (Table III). The size of R affects the rate of reaction by steric acceleration of anchimeric assistance.

A quantitative measure of the steric effect of an alkyl group on the rate of a standard reaction is avail-

(12) (a) K. Gunderman, *Angew. Chem., Int. Ed. Engl.*, **2**, 674 (1963); (b) A. G. Ogston, E. R. Holiday, J. Philpot, and L. A. Stocken, *Trans. Faraday Soc.*, **44**, 45 (1948); (c) P. D. Bartlett and C. G. Swain, *J. Amer. Chem. Soc.*, **71**, 1406 (1949); (d) R. C. Fuson, C. C. Price, and D. M. Burness, *J. Org. Chem.*, **11**, 475 (1946).

TABLE III

COUPLING CONSTANTS[a]



R	Ethers, R′ = C_2H_5, Compd	J_{AB}, Hz	Alcohols,[b] R′ = H, Compd	J_{AB}, Hz
CH_3	*erythro*-13	4.9	*erythro*-23	4.2
	threo-13	7.8	*threo*-23	7.2
C_2H_5	*erythro*-14	6.4	*erythro*-24	5.2
	threo-14	7.2	*threo*-24	6.4
i-C_3H_7	*erythro*-15	9.5	*erythro*-25	8.9
	threo-15	7.8	*threo*-25	6.7
t-C_4H_9	*erythro*-16	7.6	*erythro*-26	
	threo-16	6.8	*threo*-26	5.9
$CH(C_2H_5)_2$	*erythro*-17	9.5	*erythro*-27	8.9
	threo-17	8.4	*threo*-27	7.6
$CH_2C(CH_3)_3$	*erythro*-18	5.5	*erythro*-28	3.8
	threo-18	7.8	*threo*-28	6.5
Cyclopropyl	*erythro*-19	4.2	*erythro*-29	4.5
	threo-19	6.0	*threo*-29	
Cyclobutyl	*erythro*-20	5.7	*erythro*-30	
	threo-20	5.9	*threo*-30	5.2
Cyclopentyl	*erythro*-21	7.0	*erythro*-31	6.2
	threo-21	6.4	*threo*-31	5.2
Cyclohexyl	*erythro*-22	9.4	*erythro*-32	8.7
	threo-22	7.1	*threo*-32	5.9

[a] Spectra were determined from a mixture of about 85% ether and 15% alcohol in deuteriochloroform at ambient temperature. [b] Owing to the low concentration of alcohols, coupling constants are only considered accurate to ±0.3 Hz.

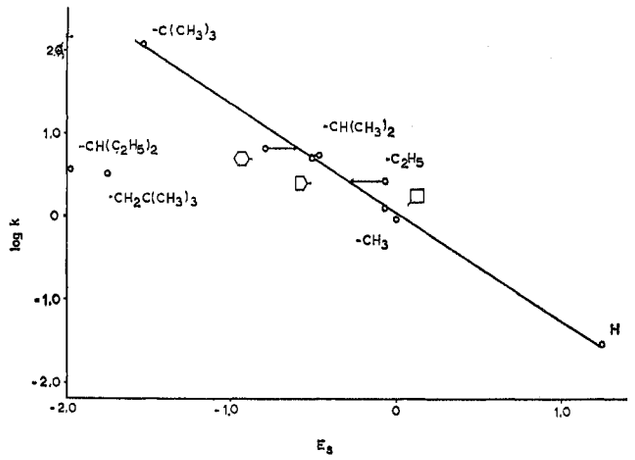
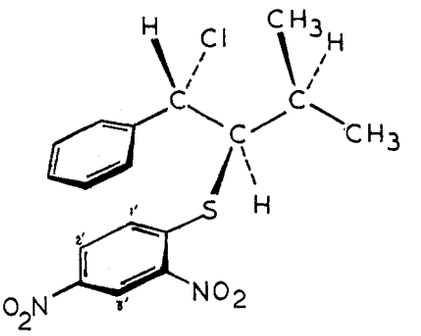


Figure 1.—Plot of the logarithm of solvolysis rate for compounds of general structure 1 (having the R groups indicated in the plot) *vs.* Taft's steric substituent constants (E_S).

able in the form of Taft's E_S values.[13] In general, the rates of solvolysis correlate adequately with E_S, although the points for certain compounds are far off the line (Figure 1). It seems quite likely that the reaction from which E_S values were defined, the hydrolysis of certain esters, was partly sensitive to the size of a substituent at its periphery. However, the degree of steric acceleration of anchimeric assistance of **2–12** is sensitive to the size of a substituent near its point of attachment to the ethanic skeleton. Thus, neopentyl, which has a huge E_S value, shows only a small conformational preference and a low reaction rate. For neopentyl, and other R groups which did not correlate with E_S, adjusted E_S values were taken (as shown by the arrows in Figure 1) essentially making all rates colinear. An E_S value for cyclopropyl was similarly determined (−0.05). Rather than the above treatment, an attempted correlation with cyclohexane conformational free energies[14] or with G values[15] would have been preferable, but data were not available for the full range of substituents.

Figure 1 shows that R = *tert*-butyl greatly accelerates the solvolysis rate, as expected from its great size. As indicated above, the probable conformation of *erythro*-**6** (R = *tert*-butyl) is different from that of other compounds having sizable groups, *e.g.*, **5** and **7**, which strongly prefer E_T. The transition state for the solvolysis resembles E_T, since the neighboring group, sulfide, is trans to the leaving group. Thus, in analogy to Curtin–Hammett considerations,[16] there is no requirement that a ground-state conformation favorable for neighboring-group assistance must be highly populated in order to observe rapid solvolysis. In fact, **5** and **7** solvolyze more slowly than **6**, though E_T is more highly populated. Numerous recent studies have correlated reactivity with ground-state conformation, and, in most cases, the data were carefully interpreted.[17] However, claims are made in certain papers that a favorable (or unfavorable) ground-state conformation is responsible for high (or low) reactivity. In our estimation, it is dubious whether ground-state conformation *per se* determines reactivity, in the absence of high barriers to conformational interconversion. Conformation and reactivity often parallel one another because both are related to the same basic factor, *i.e.*, the minimization of nonbonded interactions in the predominant ground-state conformation *and in the transition state.*

Since nothing *requires* ground-state conformation to be related in any way to solvolysis rate, a cross-check on the revised E_S values seemed advisable. This was possible through use of the chemical-shift data (Table I).[18] As the size of R increases, and E_T becomes increasingly important, an upfield shift of the aromatic hydrogens 1′–3′ is observed. This shift is most regular for 2′, which is not subject to variable steric interactions with other groups. As E_T becomes more highly populated, the preferred conformation of the dinitrophenyl groups becomes one in which this group is face to face (or, more likely, somewhat off center of face to face) with the other aromatic group (structure b).[19]



b

Thus 2′ suffers shielding owing to the ring current of the neighboring phenyl group. Models show that such shielding is also possible in E_{G1}, though less probable because the dinitrophenyl group is directed away from phenyl by R. The possibility of a intramolecular charge-transfer interaction[20] between the two rings in the face-to-face conformation was investigated by means of ^{13}C shifts. Additional electron density in the dinitrophenyl ring should result in an upfield shift. However, a downfield shift of 2.1 ppm was observed for $C_{1'}$, although upfield shifts of 1.1 ppm were noted for $C_{2'}$ and $C_{3'}$ in comparison to a compound in which

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(14) J. A. Hirsch, "Topics in Stereochemistry," Vol. I, N. L. Allinger and E. L. Eliel, Ed., Interscience, New York, N. Y., 1967, p 199.

(15) J. E. Anderson and H. Pearson, *Chem. Commun.*, 871 (1971).

(16) D. Y. Curtin, *Rec. Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **15**, 111 (1954).

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(19) (a) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); (b) J. S. Waugh and R. F. Fessenden, *J. Amer. Chem. Soc.*, **29**, 846 (1957); (c) H. O. House, R. Magin, and H. Thompson, *J. Org. Chem.*, **28**, 2403 (1963); (d) F. A. Bovey, F. Hood, E. Anderson, and L. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).

(20) (a) M. Oki and K. Mutai, *Tetrahedron*, **26**, 1181 (1970); (b) H. Craenen, J. Verhoeven, and T. deBoer, *ibid.*, **27**, 2561 (1971); *Tetrahedron Lett.*, **26**, 1167 (1970); (c) R. Carruthers, *Chem. Commun.*, 1206 (1967).

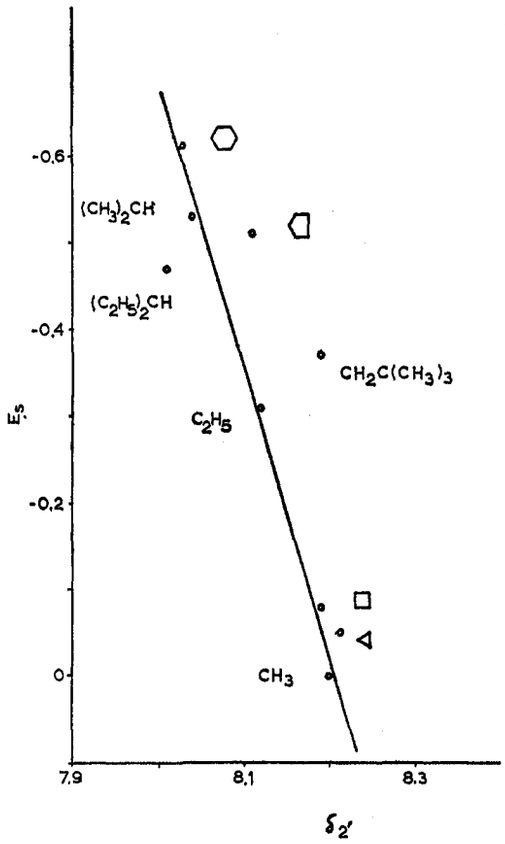


Figure 2.—Plot of corrected steric substituent constants (derived from Figure 1) *vs.* the chemical shift on the 2′ hydrogen of the dinitrophenyl ring in compounds of general structure 1 (having the various R groups indicated).

isopropyl replaced phenyl. This variation does not permit the identification of a charge-transfer interaction, although it seems likely that one should occur.

Figure 2 shows a plot of revised E_S *vs.* the chemical shift of hydrogen 2′ (observed at high dilution). The plot is fortuitously linear, though some points are well off the line. From this plot, doubly corrected values for E_S are taken (major changes include diethylcarbinyl, −0.66; neopentyl, −0.05; cyclobutyl −0.05; and cyclopropyl, +0.02).

In setting up the above-mentioned linear free energy correlation, the usual expression for the equilibrium between the (sum of) gauche conformer(s) and the trans conformer is taken (eq 2)[21]

$$K = (J_{obsd} - J_G)/(J_T - J_{obsd}) \quad (2)$$

where J_T and J_G are the limiting values expected for a conformationally pure material (*i.e.*, 100% E_T and 100% E_{G1} and/or E_{G2}, respectively). This introduces an error, since the two conformers having gauche hydrogens will not have the same limiting coupling constant, J_G. The limiting value for E_{G1} should be smaller than that for E_{G2} because of the effect of the electronegative atom trans to hydrogen in E_{G1}. However, the population of E_{G1} should be comparatively small, particularly where R is large.

(21) K. A. McLauchlan, "Magnetic Resonance," Clarendon Press, London, 1972, p 70; see also F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 70, and ref 24.

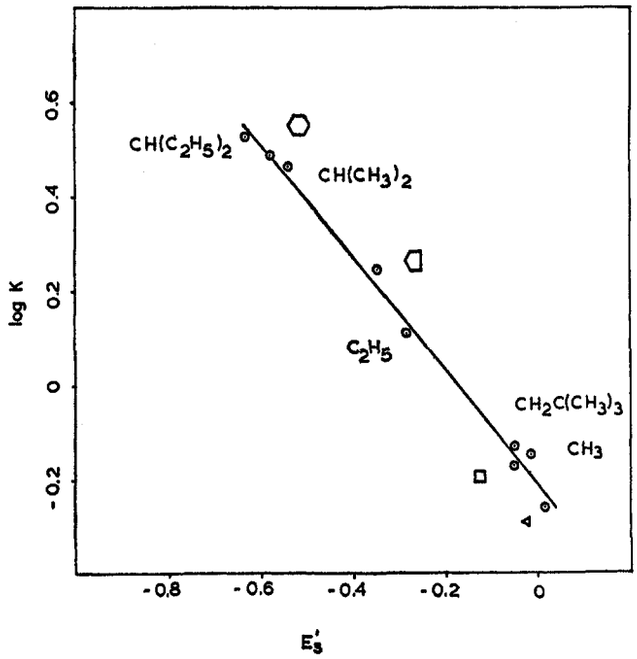


Figure 3.—Plot of the logarithm of the equilibrium constant for the conformational interconversion of trans and gauche conformers *vs.* steric substituent constants (derived from Figure 2).

For the comparison measurement

$$\Delta F^* = RT \ln (kT/hk_{rate})$$

or

$$\Delta F^* = -RT \ln k_{rate} + C \quad (3)$$

where k, T, and h have their usual significance, and where C is a constant. In comparison of the equilibrium with the data derived from rates, the linear relationship of eq 4 will be tested.

$$-RT \ln (J_{obsd} - J_G)/(J_T - J_{obsd}) = -rRT \ln k_{rate} + C'$$

or

$$\log (J_{obsd} - J_G)/(J_T - J_{obsd}) = r'E_S + C'' \quad (4)$$

Here it is convenient to use the doubly corrected E_S parameters in place of the rate constants, again redefining the constant C.

Computer-assisted analysis of eq 4 showed that a linear relationship did exist (Figure 3), but unique values for J_T and J_G could not be found by this technique. Of the various permitted solutions of eq 4 (*cf.* Appendix), that of $J_T = 13.5 \pm 1$ Hz and $J_G = 2.5 \pm 1$ Hz are considered probably closest to the true limiting values. Studies of the rigid molecule, 1-chloro-4-(1,1-dimethylpropyl)-2-cyclohexyl 2′,4′-dinitrophenyl sulfide showed a probable coupling constant of 2.1 Hz for the gauche (diequatorial) hydrogens analogous to A and B (*cf.* eq 1). However, the rigid system has the threo configuration, whereas the above analysis concerns only the erythro isomers. Also, the rigid system lacks the phenyl group. More important, deviations of the dihedral angles from the idealized value of 60° are probable, and these deviations may be quite different in the two cases. In conformer E_{G2}, a more comfortable fit of groups could be achieved by widening of the dihedral angle between vicinal hydrogens. In the cyclic molecule, the dihedral angle is probably less than

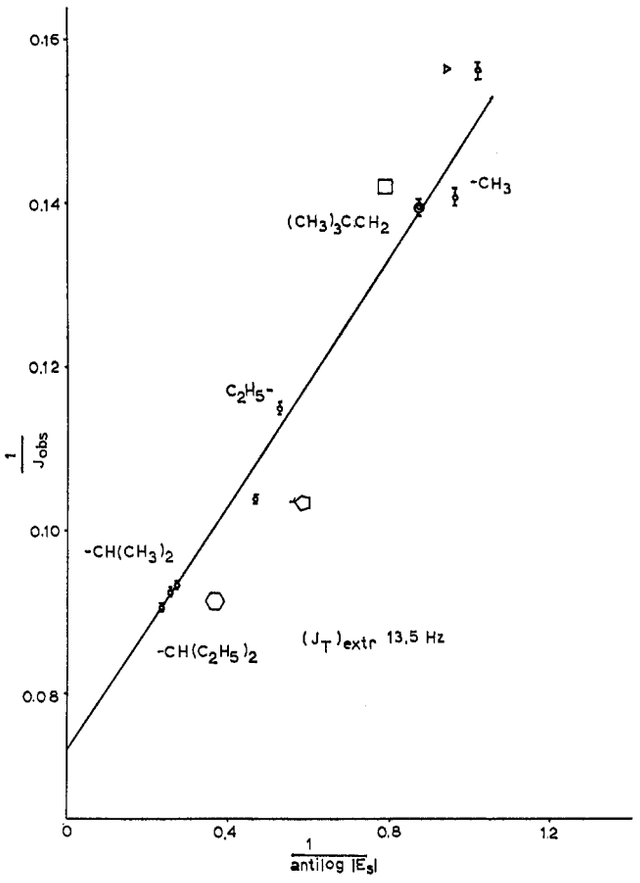


Figure 4.—Plot of the inverse of the observed nmr coupling constant *vs.* the inverse of the antilog of E_S (derived from Figure 2).

60°. Thus, there is no reason to expect exact correspondence of the limiting J values of the rigid system, and the acyclic molecules of interest, although these may be similar.

The limiting value for trans vicinal hydrogens of 13.5 Hz can be derived in a different way. A plot of $1/J_{obsd}$ *vs.* $1/a$ log E_S is fortuitously linear (Figure 4). The extrapolated value of J_{AB} is 13.5 Hz. Essentially, this treatment notes the monotonic increase in J_{AB} as the size of R increases up to *tert*-butyl, and determines the J_{AB} expected for an infinitely large R group, assuming that the linearity is maintained during the extrapolation.

Various attempts to determine the limiting coupling constants of conformers having trans or gauche hydrogens have appeared in the literature.[22] The rather common temperature-variation method now appears somewhat questionable.[23] Direct observation of the various conformers at very low temperature is in theory the best method, but it is impracticable for all but highly soluble compounds.[22c,24] A method of calculation of limiting J values from electrostatic and quadrupolar effects (resulting from solvent variation) upon observed coupling constants has been developed by Abraham, Cavelli, and Pachler.[23] This work suggests a serious drawback to our analysis, namely, that a group of compounds cannot be analyzed in terms of a single limiting value for J_T or for J_G. Each compound of a set may have its own limiting values.[6g] However, for **2–12**, only nonpolar groups are varied, and the limiting J values may all be rather similar (except[10b] for the *tert*-butyl compound **6**).[29] Unfortunately, the seriousness of this possible discrepancy is difficult to test.

In other cases, Bodot and coworkers have determined conformer populations by comparing nmr data with other experimental variables, *e.g.*, infrared spectra.[10b,24] Combinations of P–H and H–H nmr couplings have been used to estimate conformer preferences.[25] In still other cases, dipole moment data have been used in conjunction with infrared data to elucidate conformational preferences.[26] Various types of calculations have been used to determine conformational preferences, but their applicability to solution chemistry is open to question if polar groups are present.[27]

The limiting values for J_T and J_G of **2–12** may be compared to certain values from the literature. In very early work, Sheppard and Turner used 13 and 3 Hz as best values.[28] Gutowsky and coworkers favored J_T = 16 Hz, which was derived from temperature-variation measurements.[22] Whitesides and coworkers determined limiting values of *ca.* 14 and 4 Hz on certain *tert*-butyl-substituted ethanes.[29] Garbisch, Anet, and their respective coworkers determined values of *ca.* 13 and 3 Hz by direct observations on cyclohexane and its simple derivatives.[30] Altona and coworkers favored values of 9.2 and 0.9 Hz for the limiting coupling constants for the C-17 proton of a steroid and a side-chain proton[31] (a rather strained system[10b]). Eliel and coworkers determined values of *ca.* 12.5 Hz for trans diaxial protons, and 2.6–5.0 Hz for gauche (e–a) and 1.3 Hz for gauche (e–e) hydrogens in a 1,3-dioxane system, in which electronegativity effects play a large role.[32] Calculations by Fahey of limiting values in simple hydrocarbons showed J_T = 11.9 and J_G = 1.9 Hz.[33] Bodot and coworkers used values of *ca.* 10 and 2.8 Hz in calculations of conformer populations of certain chlorohydrins.[10b,33] From solvent effect studies, Abraham and coworkers calculated that J_G was 2.8 Hz in 1,1,2-trichloroethane. However, in various 1,2-dihaloethanes, J_G was of the order of 5.3 Hz when neither proton was trans to halogen but 2.5 Hz where one proton was so situated.[23] Cavanaugh used limiting

(22) (a) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1958); (b) H. S. Gutowsky, G. Belford, and P. McMahon, *ibid.*, **36**, 3353 (1962); see however, V. Tabacik, *Tetrahedron Lett.*, 555 (1968); (c) R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, **43**, 602 (1965); (d) R. A. Newmark and N. Miller, *J. Phys. Chem.*, **75**, 505 (1971); (e) See ref 6e, 10b, and 18.

(23) (a) R. J. Abraham, L. Cavelli, and K. Pachler, *Mol. Phys.*, **11**, 471 (1966); (b) R. J. Abraham and M. Cooper, *J. Chem. Soc. B*, 202 (1967); (c) see also ref 6c and 6d.

(24) J.-P. Aycard, H. Bodot, R. Garnier, R. Lauricella, and G. Pouzard, *Org. Magn. Resonance*, 7 (1970).

(25) W. G. Bentrude and K. C. Yee, *Chem. Commun.*, 169 (1972).

(26) G. Drefahl, G. Hueblein, and D. Voigt, *J. Prakt. Chem.*, **28**, 157 (1964); see also C. Altona, H. Buys, H. Hageman, and E. Havinga, *Tetrahedron*, **28**, 2273 (1967).

(27) (a) L. Radom, W. Latham, W. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **95**, 693 (1973); (b) N. L. Allinger, J. Hirsch, M. Miller, I. Tyminski, and F. Van Catledge, *ibid.*, **90**, 1199 (1968).

(28) (a) N. Sheppard and J. Turner, *Proc. Roy. Soc., Ser. A*, **252**, 506 (1959); (b) A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **84**, 743 (1962); (c) F. A. L. Anet, *ibid.*, **84**, 747 (1962).

(29) G. Whitesides, J. Sevenair, and R. Goetz, *ibid.*, **89**, 1135 (1967).

(30) (a) E. Garbisch, Jr., and M. Griffith, *ibid.*, **90**, 6543 (1968); (b) F. A. L. Anet, M. Ahmad, and L. Hall, *Proc. Chem. Soc.*, 145 (1965).

(31) (a) C. Altona and J. Hirschmann, *Tetrahedron*, **26**, 2173 (1970); (b) C. Altona and M. Sundaralingam, *ibid.*, **26**, 925 (1970).

(32) E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **11**, 739 (1972).

(33) R. C. Fahey, G. Graham, and R. Piccioni, *J. Amer. Chem. Soc.*, **88**, 193 (1966).

values of 13.5 and 2.8 Hz in studies of phenylalanine.[34] In a rigid eight-membered ring, values of J_T = 10.6 and J_G = 2.2 or 5.6 Hz were reported.[35] In an exhaustive compilation of known values of coupling constants, Bothner-By concluded that J_T was commonly in the region of 10.5–12 Hz for rigid six-membered rings, although J_T could be as low as 8 Hz for certain monosaccharides.[36]

As a check on the limiting values derived in the present study, the populations of the three conformers of compound **2** may be calculated, where x is the population of E_T, y is that of E_{G1} and, z is that of E_{G2} (R = H). Here the more proper approach is used, namely, that the coupling constant of gauche hydrogens in E_{G2} is *ca.* 2 Hz less that of E_{G1}. Since R = H in this case, two equations can be listed. Using the relationship that x, y, and z add up to 1, all variables can be found.

$$\begin{aligned} J_{obsd} &= 6.2 = 13.5x + 0.5y + 2.5z \\ J_{obsd} &= 8.5 = 2.5x + 13.5y + 0.5z \end{aligned} \quad (5)$$

The solution is x = 0.43, y = 0.55, and z = 0.02. On the other hand, if E_{G1} and E_{G2} are assumed to have the same coupling constant, 2.5 Hz, x = 0.32, y = 0.55, and z = 0.12. In either case, the least stable conformer, E_{G2}, has the lowest population, and the most sterically unhindered conformer, E_{G1}, has the highest population.

From the limiting coupling constants defined above, the percentage of E_T can be roughly calculated to be 42% for **3**, 56% for **4**, 74% for **5**, 77% for **7**, 35% for **9**, 43% for **10**, 64% for **11**, and 75% for **12**. Using another solution of eq 4, J_T = 14.5 Hz and J_G = 1.5 Hz, the population of E_T would be 43% for **3** and 73% for **7**. Using limiting values of 12.5 and 3.5 Hz, the population of E_T would be 40% for **3** and 83% for **7**. Thus, the population of E_T is not strongly sensitive to the exact solution of eq 4. Holding J_T constant and permitting J_G to vary by ±1 Hz produces a maximum variation of ±10% in the compounds having a low population of E_T. Holding J_G constant and varying J_T by ±1 Hz, produces a maximum variation of ±7% (in the compounds rich in E_T). An allowance for the different coupling constants expected for E_{G1} and E_{G2} would vary the percentages of E_T quoted by a few per cent.

Threo Isomers.—The preferred conformation of the threo isomers results from a balance of a number of factors. An increase in the size of R results in an initial decrease in J_{AB} followed by an increase, *i.e.*, the series **2** → **3** → **4** → **5** shows a minimum in J_{AB} at **4** (R = ethyl); the series **9** → **10** → **11** → **12** has a minimum at **10** (R = cyclobutyl). When R is very small, a variety of conformations are populated. As R becomes somewhat larger, a preference for T_{G1} occurs in which R and phenyl are trans. As R becomes very large, models suggest that the motion of S–Ar becomes highly restricted in T_{G1} and conformer T_T becomes somewhat more important, resulting in an increase in J_{AB}. The latter conformer permits the S–Ar group somewhat more freedom, at the expense of placing R gauche to phenyl. In agreement with the larger population of T_T in **5** and **7**, hydrogens 1′, 2′, and 3′ of the dinitrophenyl ring are relatively unshielded, since the two aromatic rings are remote from one another in T_T. *threo*-**6**, however, strongly prefers T_{G1}. Models again show that the face-to-face conformation of the aromatic rings is preferred. The resonance of 1′ (6.5 ppm) lies upfield from phenyl, owing to extreme shielding, whereas in **2**–**5** this resonance lies downfield from phenyl.

The effect of moving to a more polar solvent (DMSO) is indicated in Table I. Little solvent effect is noted for the erythro isomers. The threo isomers show a uniform increase in J_{AB}. For **5** and **11**, an increase in J_{AB} in moving to DMSO as solvent was accompanied by a decrease in J_{BC}. This change of alternate coupling constants in opposite directions is thought to reflect a true conformation change, although solvent effects on J_T and J_G may also be important.[37] Reynolds and Wood have noted similar effects of DMSO.[38] Abraham and coworkers showed that solvents complex with the various conformers to different extents, causing a change in the conformer equilibrium to favor the complexed conformer.[23] No effect of DMSO was noted in compounds lacking the C_1 phenyl group. Similar effects (though smaller) were noted in moving from $CDCl_3$ to the dipolar, but poorly hydrogen bonding solvent, acetonitrile, We tentatively suggest that a polarization interaction occurs between the dipolar solvent and the aromatic group(s), coupled with a dipolar interaction between the complexed solvent and the polar groups of the substrate. However, further study is required to elucidate why such conformers as E_{G1} are not stabilized.

Solvolysis Products.—The solvolysis of the chloro sulfides in 95% aqueous ethanol cleanly gave product ethers and alcohols of retained configuration. The coupling constants of the products were easily determined from the product mixture. No attempt was made to separate and otherwise characterize the products. The data are listed in Table III. The coupling constants for the erythro isomers are generally considerably less than those for the threo isomers. This situation is frequently met where quite strong attractive interactions exist (*e.g.*, OH–OH hydrogen bonding).[18] Only with very bulky R groups does J_{AB} for the erythro isomer exceed that for the threo isomer. As Table III shows, the preference for E_T is quite small for the erythro ethers and still smaller for the alcohols. The preference for E_{G1} and/or E_{G2} in the case of the alcohols may be due to a OH–S hydrogen bond. However, sulfur is electron deficient in **3** → **5** owing to the inductive effect of the nitro groups. These compounds show little or no tendency to complex with $Eu(dpm)_3$ or $Eu(fod)_3$.[39] This electron withdrawal would also harm hydrogen bonding.

We originally considered the possibility of an attractive oxygen–sulfur gauche interaction which occurs independently of hydrogen bonding. However, a

(34) J. R. Cavanaugh, *J. Amer. Chem. Soc.*, **92**, 1488 (1970), and earlier papers.

(35) H. Gunther, *Angew. Chem., Int. Ed. Engl.*, **11**, 861 (1972).

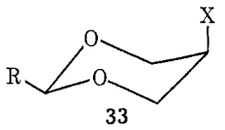
(36) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 115 (1965); see also C. Kingsbury, R. Egan, and T. Perun, *J. Org. Chem.*, **35**, 2913 (1970).

(37) (a) H. Finegold, *J. Phys. Chem.*, **72**, 3244 (1968); (b) E. I. Snyder, *J. Amer. Chem. Soc.*, **85**, 2624 (1963).

(38) W. F. Reynolds and D. Wood, *Can. J. Chem.*, **47**, 1295 (1969).

(39) (a) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); (b) P. DeMarco, T. Elzey, R. Lewis, and E. Wenkert, *ibid.*, **92**, 5743 (1970); (c) W. DeW. Horrocks, Jr., J. Sipe III, and J. Luber, *ibid.*, **93**, 5259 (1971), and references cited therein.

recent review article by Eliel indicated that the axial thio ether function X in **33** was highly destabilized,



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more so than *tert*-butyl. On the other hand, the analogous sulfoxide and sulfone groups X preferred the axial orientation.[32] Although the O–S interaction appeared unfavorable, the axial position was nearly equal in energy to the equatorial for several types of oxygen substituents.

The greater flexibility of the open-chain molecule, coupled with the fact that only one oxygen function is present, may permit gauche oxygen and sulfur groups in **13**, **14**, **18**, **19**, and **20** without the degree of repulsion between electron pairs found in **33** (X = SCH_3). In any case, the balance between all attractive and all repulsive interactions is such that these compounds will tolerate gauche OR′ and SAr groups to a considerably larger extent than gauche Cl and SAr groups (erythro isomers). According to Zefirov, electron–electron repulsions of groups having second-row atoms are substantially larger than repulsions of groups having first- and second-row atoms.[40]

Experimental Section

Compounds **2**–**12** were made by addition of 2,4-dinitrobenzenesulfenyl chloride (**34**) to the appropriate cis or trans alkene.[3,41] The alkenes were prepared by variations of the Wittig reaction.[42] The phosphonium salts, necessary for the Wittig reaction, were prepared by literature methods, and their properties were generally in accord with those reported in the literature.[42]

Preparation of Alkenes Using the Wittig Reaction (Method A.[43]—To the appropriate phosphonium salt and anhydrous potassium iodide, if used,[43] was added sufficient dry *N*,*N*-dimethylformamide (DMF) to make an approximate 1 *M* solution. The system was swept with dry nitrogen, the solution was cooled to 0–5°, and a 1 *M* solution of potassium *tert*-butoxide in dry DMF was added dropwise to the stirred mixture. An immediate red or red-orange color appeared. The addition was stopped after 1–3 ml of solution had been added. A 2 *M* solution of the appropriate aldehyde was then added dropwise until the red color disappeared. The solutions of base and aldehyde were alternately added in this manner until all aldehyde had been used, maintaining the temperature near 0°. The solution was allowed to warm to room temperature with stirring (approximately 1–2 hr), poured into water (approximately 1.1 times the volume of reaction mixture), and acidified to neutrality with dilute, aqueous HCl. The alkene was separated by extracting with petroleum ether (bp 30–60°), the combined extracts were washed with water and dried ($MgSO_4$), and the petroleum ether was removed by rotary evaporation at reduced pressure. The resulting oil was then vacuum distilled and used as the cis–trans mixture or the isomers were separated by distillation using a spinning band column or vapor phase chromatography, as indicated.

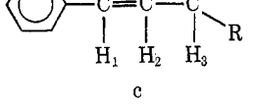
Preparation of Alkenes Using the Wittig Reaction (Method B).—The procedure used was similar to that of method A, with the exception that the base used was sodium methoxide. The base was added in small portions, in solid form (very low solubility in DMF), to the solution of phosphonium salt (and anhydrous potassium iodide, if used) until a red coloration was distinctly visible. The mixture was stirred for 2–5 min. The aldehyde solution was added dropwise, with stirring, until the red color disappeared. Alternate addition of base and aldehyde was repeated until aldehyde was exhausted. The work-up, purification, and separation of isomers were the same as in method A.

Preparation of Alkenes Using the Wittig Reaction (Method C).—To the appropriate phosphonium salt (and anhydrous potassium iodide, if used) was added enough dry DMF to make the resulting solution approximately 1 *M* in phosphonium salt. The system was swept with dry nitrogen, the solution was cooled to 0°, and a 1 *M* solution of potassium *tert*-butoxide in dry DMF was added dropwise, with stirring and cooling. When the addition was complete, a 3–5 *M* solution of aldehyde in DMF was added, dropwise, with stirring, to the reaction mixture. After stirring for an additional 2 hr, the mixture was permitted to warm to room temperature, and worked up as previously described.

Preparation of Alkenes Using the Wittig Reaction (Method D).—To the appropriate phosphonium salt (and anhydrous potassium iodide, if used) and aldehyde was added enough dry DMF to make the resulting solution approximately 1 *M* in each of the reactants. The solution was cooled to 0°, a dry nitrogen sweep was started, and a 1 *M* solution of potassium *tert*-butoxide in dry DMF was added dropwise, with stirring, maintaining the temperature near 0°. When the addition of base was complete, the mixture was stirred for 2 hr with no cooling, then worked up, and purified; the isomers were separated as discussed previously.

Addition of 2,4-Dinitrobenzenesulfenyl Chloride (34) to Alkenes. A.—A weighed amount of the appropriate alkene (usually 0.02 mol), glacial acetic acid or dry DMF (approximately 10 ml), and 2,4-DNBSC (10–50% excess) was heated on the steam bath, with swirling, for 5 min. During this time, the solid 2,4-DNBSC (**34**) dissolved. After 12–18 hr at room temperature, the solution was poured over 20 g of ice and allowed to remain until the ice had just melted. The solid obtained was separated by vacuum filtration, washed with water, and allowed to air dry. The resulting solid was recrystallized from dichloromethane–pentane or chloroform–pentane, as indicated for each compound.

B.—Alternatively, if the adduct did not crystallize upon pouring the solution over ice, the mixture was extracted with ether, washed with water, 5% sodium bicarbonate solution, and water, and dried ($MgSO_4$), and the ether was removed at reduced pressure. The resulting adduct, if it remained an oil, could be induced to crystallize by taking it up in ether–pentane. Recrystallization from appropriate solvents yielded pure adducts. In listings of parameters of the various alkenes the numbering system of structure c will be used.



c

Preparation of 1-Chloro-1-phenyl-2-ethyl 2,4-Dinitrophenyl Sulfide (2).—To a solution of styrene (8.0 g, 0.075 mol) in dry acetic acid (20 ml) was added 2,4-dinitrobenzenesulfenyl chloride (**34**) (19.0 g, 0.081 mol), yielding, after recrystallization from chloroform–pentane, 21.8 g (83%) of yellow crystals, mp 148.0° (lit.[41] mp 143.0–143.5°).

Preparation of 1-Phenyl-1-propenes Using the Wittig Reaction.—To a solution of benzyltriphenylphosphonium bromide (108.5 g, 0.25 mol) in dry DMF (250 ml) was added potassium *tert*-butoxide (50 g, 0.268 mol) in DMF (250 ml), and then acetaldehyde (12 g, 0.27 mol) in DMF (50 ml) was added according to Wittig method B. The crude oil that resulted, after work-up, was distilled using a spinning band column at reduced pressure, yielding 23 fractions of 1–1.5 ml each: fractions 2–12, bp 97–99° (82 mm); fractions 13–14, bp 100–106° (82 mm); fractions 15–23, bp 106–107° (82 mm). The fractions were analyzed by vapor phase chromatography using the QF-1 column. At a column temperature of 130° using a 60 ml/min helium flow, the retention times of the cis and trans alkenes were 6.0 and 7.25 min, respectively. Fractions 2–12 were found to be cis alkene of 99% purity, fractions 13–14 were a mixture of cis and trans alkenes, and fractions 15–23 were the trans isomer of 99% purity. The nmr spectra of these alkenes agreed with those obtained by Cabiddu, Maccioni, and Secci.[42]

(40) (a) N. S. Zefirov, V. Blagoveshchensky, I. Kazimirchik, and N. Surova, *Tetrahedron*, **27**, 3111 (1971). (b) In **13**–**20**, the nitro groups render sulfur electron deficient and reduce the size of the nonbonded pairs. Sulfur could then attract oxygen by the means noted by Pople[27a] [see also M. Robb, W. Haines, and I. Czizmadia, *J. Amer. Chem. Soc.*, **95**, 42 (1973)].

(41) (a) N. Kharasch and R. B. Longford, *Org. Syn.*, **44**, 47 (1944); (b) N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, **71**, 2724 (1949).

(42) S. Cabiddu, A. Maccioni, and M. Secci, *Ann. Chim.* (*Rome*), **54**, 1153 (1964).

(43) L. D. Bergelson and M. M. Shemyakin, *Tetrahedron*, **19**, 149 (1963).

Preparation of *erythro*-1-Chloro-1-phenyl-2-propyl 2,4-Dinitrophenyl Sulfide (3).—To *trans*-1-phenylpropene (0.58 g, 0.0049 mol) in dry acetic acid (10 ml) was added 2,4-DNBSC (**34**) (1.20 g, 0.0051 mol), yielding, after recrystallization from $CHCl_3$–pentane, 1.52 g (89%) of yellow crystals, mp 91–91.5° (lit.[44] mp 91.5–92.0°).

Anal. Calcd for $C_{15}H_{13}ClN_2O_4S$: C, 51.07; H, 3.71. Found: C, 51.11; H, 3.78.

Preparation of *threo*-1-Chloro-1-phenyl-2-propyl 2,4-Dinitrophenyl Sulfide (3).—To *cis*-1-phenylpropene (0.58 g, 0.049 mol) in dry acetic acid (10 ml) was added 2,4-DNBSC (**34**) (1.21 g, 0.0051 mol). This yielded, after recrystallization from chloroform–pentane, 1.43 g (83%) of adduct, mp 93.5–94.5°.

Anal. Calcd for $C_{15}H_{13}ClN_2O_4S$: C, 51.07; H, 3.71. Found: C, 51.20; H, 3.59.

Preparation of 1-Phenyl-1-butenes.—The procedure of Wittig method A was followed using benzyltriphenylphosphonium bromide (108 g, 0.25 mol) and anhydrous potassium iodide (83 g) in DMF (250 ml), and alternately adding potassium *tert*-butoxide (50 g, 0.268 mol) in DMF (300 ml) and propanal (16 g, 0.275 mol) in DMF (80 ml). The reaction yielded 27 g (82%) of a slightly yellow oil which was distilled, using a spinning band column, yielding 21 fractions of 0.5–1.5 ml each: fractions 1–3, bp 22–80° (20 mm); fractions 4–15, bp 80–83° (20 mm); fractions 16–17, bp 84–89° (20 mm); fractions 18–21, bp 89–91° (20 mm) [lit.[44] cis alkene bp 84.0–85.0° (23 mm); trans alkene, 91.0–92.0° (23 mm)]. The nmr of fractions 8 and 20 showed then to be *cis*- and *trans*-1-phenyl-1-butene, respectively.

cis-1-Phenyl-1-butene had nmr (CCl_4) δ 1.05 (t, 3, J_{CH_2,CH_3} = 7.5 Hz, CH_3), 2.00–2.60 (m, 2, CH_2), 5.57 (dt, 1, J_{2,CH_2} = 7.0 Hz, $J_{1,2}$ = 11.6 Hz, H_2), 6.33 (dt, 1, $J_{1,2}$ = 11.6 Hz, J_{1,CH_2} = 1.6 Hz, H_1), 7.05–7.30 (m, 5, aromatic protons).

trans-1-phenyl-1-butene had nmr (CCl_4) δ 1.09 (t, 3, J_{CH_2,CH_3} = 7.5 Hz, CH_3), 1.90–2.50 (m, 2, CH_2), 5.80–6.50 (m, 2, H_1 and H_2), 7.00–7.40 (m, 5, aromatic protons).

Preparation of *erythro*-1-Chloro-1-phenyl-2-butyl 2,4-Dinitrophenyl Sulfide (4).—To *trans*-1-phenyl-1-butene (1.53 g, 0.01 mol) in DMF (10 ml) was added **34** (2.65 g, 0.0108 mol). After recrystallization from dichloromethane–pentane, there resulted 3.21 g (88%) of pure adduct, mp 144.0–144.5° (lit.[45] mp 144.4–144.8°).

Anal. Calcd for $C_{16}H_{15}ClN_2O_4S$: C, 52.39; H, 4.12. Found: C, 52.24; H, 4.08.

Preparation of *threo*-4.—To *cis*-1-phenyl-1-butene (1.31 g, 0.01 mol) in DMF (10 ml) was added **34** (2.68 g, 0.0109 mol). Recrystallization from dichloromethane–pentane yielded 3.62 g (76%) of pure adduct: mp 127.0–127.5°; nmr δ 1.15 (t, 3, J_{CH_3,CH_2} = 7.2 Hz, CH_3), 1.60–2.50 (m, 2, CH_2), 3.87 (dt, 1, J_{2,CH_2} = 8.5, $J_{1,2}$ = 4.8 Hz, H_2), 5.27 (d, 1, $J_{1,2}$ = 4.8 Hz, H_1), 7.15–7.65 (m, 6, aromatic protons and $H_{1'}$), 8.21 (dd, 1, $J_{1',2'}$ = 8.9, $J_{2',3'}$ = 2.5 Hz, $H_{2'}$), 8.91 (d, 1, $J_{2',3'}$ = 2.5 Hz, $H_{3'}$).

Anal. Calcd for $C_{16}H_{15}ClN_2O_4S$: C, 52.39; H, 4.12. Found: C, 52.28; H, 4.26.

Preparation of 3-Methyl-1-phenyl-1-butenes. A.—The procedure of Wittig method C was followed using benzyltriphenylphosphonium bromide (108 g, 0.25 mol) and anhydrous potassium iodide (83.0 g, 0.5 mol) in DMF (270 ml). To this was added potassium *tert*-butoxide (50 g, 0.268 mol) in DMF (360 ml), followed by a solution of 2-methylpropanal (19.8 g, 0.275 mol) in DMF (50 ml). The reaction yielded 39.3 g (89.5%) of a slightly yellow oil, which, the nmr spectrum indicated, consisted of a mixture of 89% cis alkene and 11% trans alkene. The mixture was used without further purification.

B.—The procedure of Wittig method D was followed using isobutyltriphenylphosphonium iodide (111.5 g, 0.25 mol), benzaldehyde (26.5 g, 0.25 mol) in DMF (300 ml), and potassium *tert*-butoxide (50 g, 0.268 mol) in DMF (200 ml). The resulting oil was distilled, using a spinning band column, yielding 13 fractions (*ca.* 2 ml each): fractions 2–7, bp 76–77° (12 mm); fractions 8–9, bp 77–83° (12 mm); fractions 10–13, bp 84–85° (12 mm). These fractions were analyzed by vapor phase chromatography using the QF-1 column. At a column temperature of 155° and 60 ml/min helium flow, the retention times of the cis and trans alkenes were 3.25 and 4.75 min, respectively.

cis-3-Methyl-1-phenyl-1-butene had nmr (94 mg of alkene/744 mg of CCl_4) δ 1.02 (d, 6, J_{3,CH_3} = 6.5 Hz, CH_3), 2.50–3.30 (m, 1, H_3), 5.39 (dd, 1, $J_{1,2}$ = 11.6, $J_{2,3}$ = 9.95 Hz, H_2), 6.25 (d, 1, $J_{1,2}$ = 11.6 Hz, H_1), 7.18 (s, 5, aromatic protons).

trans-3-Methyl-1-phenyl-1-butene had nmr (139 mg of alkene/1.12 g of CCl_4) δ 1.06 (d, 6, J_{3,CH_3} = 6.3 Hz, CH_3), 2.15–2.85 (m, 1, H_3), 5.80–6.50 (m, 2, H_1 and H_2), 6.95–7.35 (m, 5, aromatic protons).

Preparation of *erythro*-1-Chloro-3-methyl-1-phenyl-2-butyl 2,4-Dinitrophenyl Sulfide (5).—To *trans*-3-methyl-1-phenyl-1-butene (2.86 g, 0.019 mol) in acetic acid (10 ml) was added **34** (4.71 g, 0.02 mol). The adduct, after recrystallization from chloroform–pentane, weighed 6.92 g (93%), mp 161–162°.

Anal. Calcd for $C_{17}H_{17}ClN_2O_4S$: C, 53.61; H, 4.50. Found: C, 53.68; H, 4.57.

Preparation of *threo*-5.—To the solution of a mixture of *cis*- and *trans*-3-methyl-1-phenyl-1-butene (89% cis, 11% trans alkene; 3.1 g, 0.0212 mol) in DMF (10 ml) was added **34** (5.3 g, 0.0225 mol). The mixture of diastereomers resulting from this reaction was separated by fractional recrystallization from chloroform–pentane, yielding 5.83 g (75%) of pure threo diastereomer, mp 137.5–138°.

Anal. Calcd for $C_{17}H_{17}ClN_2O_4S$: C, 53.61; H, 4.50; N, 7.36. Found: C, 53.62; H, 4.36; N, 7.39.

Preparation of *erythro*-1-Chloro-3,3-dimethyl-1-phenyl-2-butyl 2,4-Dinitrophenyl Sulfide (6).—To a solution of *trans*-3,3-dimethyl-1-phenyl-1-butene (1.0 g, 6.25 mmol) in acetic acid (10 ml) was added **34** (1.65 g, 7.0 mmol). The yield, after recrystallization from chloroform–pentane, was 1.67 g (68%), mp 134.0–134.5°.

Anal. Calcd for $C_{18}H_{10}ClN_2O_4S$: C, 54.75; H, 4.85. Found: C, 54.85; H, 4.85.

Preparation of *threo*-6.—To a solution of *cis*-3,3-dimethyl-1-phenyl-1-butene (1.0 g, 6.25 mmol) in acetic acid (10 ml) was added **34** (1.66 g, 7.0 mmol). There was obtained 1.96 g (79%) of yellow needles, mp 142.5–143.0° (chloroform–pentane).

Anal. Calcd for $C_{18}H_{19}ClN_2O_4S$: C, 54.75; H, 4.85; N, 7.09. Found: C, 54.76; H, 4.72; N, 7.22.

Preparation of 3-Ethyl-1-phenyl-1-pentenes.—The procedure of Wittig method A was followed using benzyltriphenylphosphonium bromide (108 g, 0.25 mol) in DMF (200 ml). To this solution was added, alternately, solutions of potassium *tert*-butoxide (50 g, 0.268 mol) in DMF (325 ml) and 2-ethylbutanal (27.7 g, 0.252 mol) in DMF (50 ml). The reaction yielded 35.2 g (81%) of an oil with bp 64–69° (0.14 mm). This liquid was distilled, using a spinning band column, and yielded 17 fractions of 2–3 ml each: fractions 1–9, bp 87–89° (3.1 mm); fractions 10–11, bp 89.5–39° (3.1 mm); fractions 12–17, bp 90–93° (2.9–3.0 mm).

cis-3-Ethyl-1-phenyl-1-pentene (fractions 1–9) had nmr (neat liquid) δ 0.65–1.05 (m, 6, CH_3), 0.65–1.70 (m, 4, CH_2), 2.15–2.75 (m, 1, H_3), 5.32 (dd, 1, $J_{2,3}$ = 10.5, $J_{1,2}$ = 12.0 Hz, H_2), 6.50 (d, 1, $J_{1,2}$ = 12.0 Hz, H_1), 6.95–7.35 (m, 5, aromatic protons).

trans-3-Ethyl-1-phenyl-1-pentene (fractions 12–17) had nmr (neat liquid) δ 0.65–1.05 (m, 6, CH_3), 1.05–2.20 (m, 5, CH_2 and H_3), 5.87 (dd, 1, $J_{2,3}$ = 7.7, $J_{1,2}$ = 16.0 Hz, H_2), 6.30 (d, $J_{1,2}$ = 16.0 Hz, H_1), 7.00–7.40 (m, 5, aromatic protons).

Preparation of *erythro*-1-Chloro-3-ethyl-1-phenyl-2-pentyl 2,4-Dinitrophenyl Sulfide (7).—To a solution of *trans*-3-ethyl-1-phenyl-1-pentene (1.76 g, 0.01 mol) in DMF (10 ml) was added **34** (2.59 g, 0.015 mol), yielding 3.66 g (90%) of yellow crystals, mp 161.1–161.7°, after recrystallization from dichloromethane–pentane.

Anal. Calcd for $C_{19}H_{21}ClN_2O_4S$: C, 55.81; H, 5.18. Found: C, 55.82; H, 5.05.

Preparation of *threo*-7.—To a solution of *cis*-3-ethyl-1-phenyl-1-pentene (1.74 g, 0.01 mol) in DMF (10 ml) was added **34** (2.60 g, 0.015 mol), yielding 3.41 g (83%) of recrystallized adduct, mp 115.5–116.0° (dichloromethane–pentane). Interpretation of the nmr spectrum was made difficult by the fact that the four methylene protons of the two ethyl groups and H_3 all had essentially the same chemical shift, causing extensive virtual coupling. The absorbance for H_2 was therefore very broad and an exact value for $J_{2,3}$ was impossible to obtain. Computer simulation of the spectrum showed that the best value for this coupling constant was *ca.* 4 ± 1 Hz.

Anal. Calcd for $C_{19}H_{21}ClN_2O_4S$: C, 55.81; H, 5.18. Found: C, 55.82; H, 5.09.

Preparation of 4,4-Dimethyl-1-phenyl-1-pentenes.—The procedure of Wittig method D was followed, using a solution of 3,3-dimethylbutyltriphenylphosphonium bromide (171 g, 0.40 mol)

(44) T. DeWolfe, D. Hagman, and W. G. Young, *J. Amer. Chem. Soc.*, **79**, 4795 (1957).

(45) C. F. Hauser, T. Brooks, M. Miles, M. Raymond, and G. B. Butler, *J. Org. Chem.*, **28**, 372 (1963).

and benzaldehyde (45 g, 0.425 mol) in 600 ml of DMF and adding a solution of potassium *tert*-butoxide (75 g, 0.4 mol) in DMF (500 ml). The reaction yielded 81.3 g (80%) of a clear liquid, bp 52–58° (0.12 mm). The resulting oil was distilled, using a spinning band column, yielding 16 fractions: fractions 2–6, bp 90.5–92.5° (5 mm); fractions 6–8, bp 92.5–98° (5 mm); fractions 8–16, bp 98.0–99.5° (5 mm).

cis-4,4-Dimethyl-1-phenyl-1-pentene (fractions 2–6) had nmr δ 0.89 (s, 9, *tert*-butyl protons), 2.24 (dd, 2, J_{2,CH_2} = 7.4 Hz, J_{1,CH_2} = 1.8 Hz, CH_2), 5.77 (dt, 1, J_{2,CH_2} = 7.4 Hz, $J_{1,2}$ = 12.2 Hz, H_2), 6.53 (dt, 1, $J_{1,2}$ = 12.2 Hz, J_{1,CH_2} = 1.8 Hz, H_1), 7.05–7.40 (m, 5, aromatic protons).

trans-4,4-Dimethyl-1-phenyl-1-pentene (fractions 8–16) had nmr (neat liquid) δ 0.92 (s, 9, *tert*-butyl protons), 1.90–2.15 (m, 2, CH_2), 5.85–6.55 (m, 2, H_1 and H_2), 7.00–7.40 (m, 5, aromatic protons).

Preparation of *erythro*-1-Chloro-4,4-dimethyl-1-phenyl-2-pentyl 2,4-Dinitrophenyl Sulfide (8).—To a solution of *trans*-4,4-dimethyl-1-phenyl-1-pentene (1.77 g, 0.01 mol) in DMF (10 ml) was added **34** (2.58 g, 0.015 mol), yielding, after recrystallization from dichloromethane–pentane, 3.62 g (89%) of yellow needles, mp 115.5–116°.

Anal. Calcd for $C_{19}H_{21}ClN_2O_4S$: C, 55.81; H, 5.18. Found: C, 55.99; H, 5.22.

Preparation of *threo*-8.—To a solution of *cis*-4,4-dimethyl-1-phenyl-1-pentene (1.74 g, 0.01 mol) in acetic acid (10 ml) was added **34** (2.60 g, 0.015 mol), yielding 3.38 g (83%) of crude adduct, which, the nmr spectrum indicated, consisted of a mixture of Markovnikov and anti-Markovnikov addition products. The reaction was repeated in DMF with similar results. The mixture consisted of 54% *threo*-1-chloro-4,4-dimethyl-1-phenyl-2-pentyl 2,4-dinitrophenyl sulfide [Markovnikov addition product, with a doublet at δ 5.23 (J = 4.3 Hz) and a multiplet at δ 3.94] and 46% 2-chloro-4,4-dimethyl-1-phenyl-1-pentyl 2′,4′-dinitrophenyl sulfide [anti-Markovnikov addition product, with a doublet at δ 4.76 (J = 4.5 Hz) and a multiplet at δ 4.37]. The mixture was fractionally recrystallized from dichloromethane–petroleum ether, affording pure Markovnikov product, 1.37 g (33%), mp 152.8–153.1°.

Anal. Calcd for $C_{19}H_{21}ClN_2O_4S$: C, 55.81; H, 5.18. Found: C, 55.86; H, 5.15.

Preparation of 1-Cyclopropyl-2-phenylethylene.—The procedure of Wittig method A was followed, using a solution of benzyltriphenylphosphonium bromide (129 g, 0.30 mol) in DMF (300 ml), and adding, alternately, solutions of potassium *tert*-butoxide (57 g, 0.03 mol) in DMF (250 ml) and cyclopropanecarboxaldehyde (20.52 g,) The reaction yielded, upon distillation, 34.8 g of a clear, colorless oil, bp 54.0–64.5° (0.18–2.4 mm). The oil was spinning band distilled, yielding 22 fractions of 1–2 ml each: fractions 1–10, bp 60.5–61.5° (0.5 mm); fractions 11–12, bp 61.5–66.5° (0.5 mm); fractions 13–22, bp 67.0–69.0° (0.5 mm). The nmr spectra are in agreement with those reported by Schweizer, Thompson, and Ulrich.[46]

cis-1-Cyclopropyl-2-phenylethylene (fraction 9) had nmr (neat liquid) δ 0.15–0.80 (m, 4, $-CH_2-$ of ring), 1.48–2.14 (m, 1, H_3), 4.96 (dd, 1, $J_{2,3}$ = 9.6, $J_{1,2}$ = 11.6 Hz, H_2), 6.35 (d, 1, $J_{1,2}$ = 11.6 Hz, H_3), 7.0–7.5 (m, 5, aromatic protons).

trans-1-Cyclopropyl-2-phenylethylene (fraction 16) had nmr (neat liquid) δ 0.15–0.85 (m, 4, $-CH_2-$ of ring), 1.05–1.70 (m, 1, H_3), 5.62 (dd, 1, $J_{2,3}$ = 8.4, $J_{1,2}$ = 16.0 Hz, H_2), 6.35 (d, 1, $J_{1,2}$ = 16.0 Hz, H_1), 6.90–7.35 (m, 5, aromatic protons).

Preparation of *erythro*-1-Chloro-2-cyclopropyl-1-phenyl-2-ethyl 2,4-Dinitrophenyl Sulfide (9).—To a solution of *trans*-1-cyclopropyl-2-phenylethylene (1.47 g, 0.01 mol) in DMF (10 ml) was added **34** (2.62 g, 0.011 mol). The solution was heated briefly (1–2 min) until **34** went into solution, and then allowed to stand at room temperature for 8 days before work up. From the reaction was obtained 3.19 g (82%) of yellow needles, mp 147.2–147.8° (dichloromethane–pentane).

Anal. Calcd for $C_{17}H_{15}ClN_2O_4S$: C, 53.90; H, 3.99. Found: C, 53.80; H, 3.93.

Preparation of *threo*-9.—To a solution of *cis*-1-cyclopropyl-2-phenylethylene (1.45 g, 0.01 mol) in DMF (10 ml) was added **34** (2.62 g, 0.011 mol). The mixture was allowed to stand, without heating, for 31 days at room temperature. From this reaction was obtained 2.66 g (70%) of yellow needles, mp 141.8–142.1° (dichloromethane–pentane).

(46) E. Schweizer, J. Thompson, and F. Ulrich, *J. Org. Chem.*, **33**, 3082 (1968).

Anal. Calcd for $C_{17}H_{15}ClN_2O_4S$: C, 53.90; H, 3.99. Found: C, 54.00; H, 3.98.

Preparation of 1-Cyclobutyl-2-phenylethylene.—The procedure was that of Wittig method A using a solution of benzyltriphenylphosphonium bromide (119 g, 0.275 mol) in DMF (300 ml) and alternately adding solutions of potassium *tert*-butoxide (56 g, 0.30 mol) in DMF (300 ml) and cyclobutanecarboxaldehyde (23.1 g, 0.275 mol). From the reaction was obtained 25.3 g (58%) of an oil with bp 115–120° (9–10 mm). This product was analyzed and the isomers were separated by vapor phase chromatography using the QF-1 column. From 26 injections of 20–30 μl each were collected 133 mg of cis alkene and 84 mg of trans alkene. At a column temperature of 185°, using a 60 ml/min helium flow, the retention times of the cis and trans alkenes were 3.15 and 4.20 min, respectively.

cis-1-Cyclobutyl-2-phenylethylene had nmr ($CDCl_3$) δ 1.70–2.50 (m, 6, $-CH_2-$ of ring), 3.05–3.80 (m, 1, H_3), 5.81 (dd, 1, $J_{2,3}$ = 8.8, $J_{1,2}$ = 11.6 Hz, H_2), 6.33 (dd, 1, $J_{1,2}$ = 11.6, $J_{1,3}$ = 0.7 Hz, H_1), 7.10–7.50 (m, 5, aromatic protons).

trans-1-Cyclobutyl-2-phenylethylene had nmr ($CDCl_3$) δ 1.50–2.50 (m, 6, $-CH_2-$ of ring), 2.75–3.45 (m, 1, H_3), 6.25–6.45 (m, 2, H_2 and H_3), 7.00–7.60 (m, 5, aromatic protons).

Preparation of *erythro*-1-Chloro-2-cyclobutyl-1-phenyl-2-ethyl 2,4-Dinitrophenyl Sulfide (10).—To a solution of *trans*-1-cyclobutyl-2-phenylethylene (85 mg, 5.3 mmol) in DMF (2 ml) was added **34** (140 mg, 6.0 mmol), yielding 183 mg (88%) of yellow crystals, mp 104.5–105.0° (dichloromethane–petroleum ether).

Anal. Calcd for $C_{18}H_{17}ClN_2O_4S$: C, 55.03; H, 4.36. Found: C, 54.95; H, 4.30.

Preparation of *threo*-10.—To a solution of *cis*-1-cyclobutyl-2-phenylethylene (133 mg, 8.4 mmol) in DMF (2 ml) was added **34** (215 mg, 9.2 mmol), yielding 259 mg (78%) of yellow crystals, mp 105.0–105.5° (ether–pentane).

Anal. Calcd for $C_{18}H_{17}ClN_2O_4S$: C, 55.03; H, 4.36. Found: C, 55.03; H, 4.33.

Preparation, Rearrangement, and Separation of Isomeric Mixture of 2,4-DNBSC Adducts to *cis*- and *trans*-1-Cyclobutyl-2-phenylethylene.—To a solution of a mixture of *cis*- and *trans*-1-cyclobutyl-2-phenylethylene (3.16 g, 0.02 mol) in dry acetic acid (10 ml) was added **34** (5.15 g, 0.022 mol), yielding 6.97 g (89%) of a yellow-brown oil which could not be induced to crystallize. The nmr spectrum of the product oil indicated that the mixture consisted of threo and erythro adducts in the ratio of approximately 6:4, plus small amounts of impurities. The oil was placed on a 2 × 60 cm Florisil column and eluted with petroleum ether, 4:1 petroleum ether–benzene, 7:3 petroleum ether–benzene, 1:1 petroleum ether–benzene, 2:3 petroleum ether–benzene, 9:1 petroleum ether–ether, 4:1 petroleum ether–ether, 1:1 petroleum ether–ether, ether, dichloromethane, ethyl acetate, and acetone. From the 4:1 petroleum ether–benzene fractions, 2.34 g of a yellow oil was obtained. The oil solidified upon standing, and was recrystallized from ether–petroleum ether, yielding 2.15 g (27.4%) of yellow crystals, mp 105.0–105.5°. This was identified, by nmr and melting point as *threo*-1-chloro-2-cyclobutyl-1-phenyl-2-ethyl 2,4-dinitrophenyl sulfide (**10**).

From the 7:3 petroleum ether–benzene fractions was obtained 2.11 g of a yellow brown oil which solidified upon standing. When recrystallized from ether–petroleum ether, there was obtained 1.98 g (25.3%) of *erythro*-2-chloro-1-cyclobutyl-2-phenyl-1-ethyl 2,4-dinitrophenyl sulfide (anti-Markovnikov adduct **10′**) as light yellow needles: mp 111.5–112.0°; nmr δ 1.60–2.25 (m, 6, $-CH_2-$ of ring), 2.50–3.10 (m, 1, H_3), 4.24 (dd, 1, $J_{2,3}$ = 8.4, $J_{1,2}$ = 5.4 Hz, H_2), 4.67 (d, 1, $J_{1,2}$ = 5.4 Hz, H_1), 7.22–7.68 (m, 6, aromatic protons and $H_{1'}$), 8.15 (dd, 1, $J_{1',2'}$ = 8.8, $J_{2',3'}$ = 2.5 Hz, $H_{2'}$), 8.96 (d, 1, $J_{2,'3'}$ = 2.5 Hz, H_3).

Anal. Calcd for $C_{18}H_{17}ClN_2O_4S$: C, 55.03; H, 4.36. Found: C, 54.95; H, 4.24.

From the 9:1 petroleum ether–ether fractions there was obtained 1.56 g of yellow oil. This was induced to crystallize from ether–petroleum ether, yielding 1.48 g (18.8%) of brilliant yellow flakes, mp 124.7–125.0°, apparently the threo anti-Markovnikov isomer (**10′**) (see below): nmr δ 1.60–2.90 (m, 7, $-CH_2-$ of ring and H_3), 3.84 (dd, 1, $J_{2,3}$ = 9.2, $J_{1,2}$ = 4.5 Hz, H_2), 5.00 (d, 1, $J_{1,2}$ = 4.5 Hz, H_1), 7.15–7.50 (m, 5, aromatic protons), 7.98 (d, 1, $J_{1,'2'}$ = 8.9 Hz, $H_{1'}$), 8.26 (dd, 1, $J_{1,'2'}$ = 8.9, $J_{1,'2'}$ = 2.5 Hz, $H_{2'}$), 8.82 (d, 1, $J_{1,'2'}$ = 2.5 Hz, $H_{3'}$).

Anal. Calcd for $C_{18}H_{17}ClN_2O_4S$: C, 55.03; H, 4.36. Found: C, 54.97; H, 4.30.

Although some yellow color was observed to remain on the column, elution by ether, dichloromethane, ethyl acetate, or acetone failed to remove the colored material completely. The yellow-brown oil material that was eluted by these solvents (total 0.97 g) failed to show, in the nmr spectra, peaks characteristic of the final desired product, *erthro*-**10**. The eluted material would not crystallize, had a foul odor, and was unidentifiable by nmr, showing only broad absorptions in the aliphatic and aromatic regions, 0.6–2.8 and 7.0–7.8 ppm, respectively.

Rearrangement of *threo*-1-Chloro-2-cyclobutyl-1-phenyl-2-ethyl 2,4-Dinitrophenyl Sulfide (10) to *threo*-1-Chloro-1-cyclobutyl-2-phenyl-2-ethyl 2,4-Dinitrophenyl Sulfide (10′).—On a 1 × 15 cm Florisil column was placed the threo Markonikov adduct (0.620 g, 1.57 mmol). After 2 days, the column was eluted with 4:1 petroleum ether–benzene and yielded 0.407 g (65.8%) of yellow crystals indentified by nmr and melting point as the Markovnikov adduct as originally placed on the column. Continued elution by 9:1 petroleum ether–ether yielded 0.203 g (32.8%) of bright yellow flakes mp 123–124°. The nmr of this latter compound was identical with that of the compound obtained from the large column using the same eluents.

Preparation of 1-Cyclopentyl-2-phenylethylenes.—The procedure of Wittig method A was followed, using a solution of benzyltriphenylphosphonium bromide (108 g, 0.25 mol) and potassium iodide (83 g, 0.50 mol) in DMF (300 ml). To this solution was added, alternately, solutions of potassium *tert*-butoxide (50 g, 0.268 mol) in DMF (250 ml) and cyclopentanecarboxaldehyde (26.5 g, 0.25 mol) in DMF (25 ml). The product was vacuum distilled, yielding 30.2 g (75.2%) of a clear oil, bp 78–79° (0.25 mm). The oil was distilled, using the spinning band column, yielding 24 fractions of 1–2 ml each: fractions 3–11, bp 86–88° (0.9 mm); fractions 12–13, bp 90–94° (1.0–1.1 mm); fractions 14–24, bp 92–96° (0.9–1.1 mm).

cis-1-Cyclopentyl-2-phenylethylene (fractions 3–11) had nmr (neat liquid) δ 1.0–2.1 (m, 8, $-CH_2-$ of ring), 2.55–3.40 (m, 1, H_3), 5.53 (dd, 1, $J_{2,3}$ = 9.8 $J_{1,2}$ = 11.6 Hz, H_2), 6.37 (d, 1, $J_{1,2}$ = 11.6 Hz, H_1), 6.80–7.40 (m, 5, aromatic protons).

trans-1-Cyclopentyl-2-phenylethylene (fractions 14–24) had nmr (neat liquid) δ 1.0–2.1 (m, 8, $-CH_2-$ of ring), 2.1–2.9 (m, 1, H_3), 5.85–6.60 (m, 2, H_1 and H_2), 7.05–7.45 (m, 5, aromatic protons).

Preparation of *erythro*-1-Chloro-2-cyclopentyl-1-phenyl-2-ethyl 2,4-Dinitrophenyl Sulfide (11).—To a solution of *trans*-1-cyclopentyl-2-phenylethylene (1.71 g, 0.01 mol) in DMF (10 ml) was added **34** (2.61 g, 0.011 mol), affording 3.75 g (92%) of yellow crystals, mp 148.5–148.7° (dichloromethane–pentane).

Anal. Calcd for $C_{19}H_{19}ClN_2O_4S$: C, 56.09; H, 4.71. Found: C, 55.95; H, 4.67.

Preparation of *threo*-11.—To a solution of *cis*-1-cyclopentyl-2-phenylethylene (1.72 g, 0.01 mol) in DMF (10 ml) was added **34** (2.60 g, 0.011 mol), producing 3.51 g (86%) of yellow needles, mp 109.0–109.5° (dichloromethane–pentane).

Anal. Calcd for $C_{19}H_{19}ClN_2O_4S$: C, 56.09; H, 4.71. Found: C, 55.97; H, 4.73.

Preparation of 1-Cyclohexyl-2-phenylethylene.—The procedure of Wittig method B was followed, using a solution of benzyltriphenylphosphonium bromide (108 g, 0.25 mol) and potassium iodide (83 g, 0.50 mol) in DMF (300 ml). To this was alternately added sodium methoxide (13.5 g, 0.25 mol) and a solution of cyclohexanecarboxaldehyde (28 g, 0.25 mol) in DMF (100 ml). The crude product oil from this reaction, weighing 26 g (56%), was distilled using a spinning band column, yielding 12 fractions of 1–3 ml each: fractions 3–5, bp 98–101° (2.55 mm); fraction 6, bp 101–103° (2.50–2.55 mm); fractions 7–11, bp 103–108° (2.45–2.50 mm).[46] These fractions were analyzed by vapor phase chromatography using the QF-1 column. At a column temperature of 200° using a helium flow of 75 ml/min, the cis and trans alkenes had retention times of 2.57 and 3.48 min, respectively.

cis-1-Cyclohexyl-2-phenylethylene had nmr ($CDCl_3$) δ 0.80–2.20 (m, 10, $-CH_2-$ of ring), 2.20–3.00 (m, 1, H_3), 5.43 (dd, 1, $J_{2,3}$ = 9.6, $J_{1,2}$ = 11.6 Hz, H_2), 6.28 (d, 1, $J_{1,2}$ = 11.6 Hz, H_1), 6.85–7.40 (m, 5, aromatic protons).

trans-1-Cyclohexyl-2-phenylethylene had nmr (neat liquid) δ 0.80–2.35 (m, 11, $-CH_2-$ of ring and H_3), 5.83–6.50 (m, 2, H_1 and H_2), 6.95–7.45 (m, 5, aromatic protons).

Preparation of *erythro*-1-Chloro-2-cyclohexyl-1-phenyl-2-ethyl 2,4-Dinitrophenyl Sulfide (12).—To a solution of *trans*-1-cyclohexyl-2-phenylethylene (1.86 g, 0.01 mol) in acetic acid (10 ml) was added **34** (2.58 g, 0.011 mol), yielding 3.83 g (89%) of yellow needles, mp 173.5–174.0° (dichloromethane–pentane).

Anal. Calcd for $C_{20}H_{21}ClN_2O_4S$: C, 57.07; H, 5.03. Found: C, 56.97; H, 5.12.

Preparation of *threo*-12.—To a solution of *cis*-1-cyclohexyl-2-phenylethylene (1.86 g, 0.01 mol) in acetic acid (10 ml) was added **34** (2.58 g, 0.011 mol), yielding 3.76 g (87%) of yellow needles, mp 139.0–139.5° (dichloromethane–pentane).

Anal. Calcd for $C_{20}H_{21}ClN_2O_4S$: C, 57.07; H, 5.03. Found: C, 56.94; H, 5.13.

Solvolysis of 2,4-DNBSC Derivatives of the β-Substituted Styrenes.—The 2,4-DNBSC derivatives or the β-substituted styrenes were solvolyzed in aqueous ethanol (*ca.* 95%). Commercial absolute ethanol was distilled from magnesium ethoxide, taking the center cut, and diluted to desired density with dionized, triple-distilled water.

It was necessary to prepare the solvent twice. The first 5-l. quantity (solvent A) had density 0.80116 g/ml (28.4°, average of five determinations), and the second quantity of 9 l. (solvent B) had density 0.80096 g/ml (28.4°, average of six determinations). The ethanolysis rates of two compounds were determined in both solvents. It was found that the rates of B had to be multiplied by a factor of 1.0610 and 1.0609, respectively, to obtain the rate values received using solvent A. The lower of these two factors, 1.0609, was used for the rate correction of subsequent kinetics runs. Rates were determined conductiometrically, using a calibrated Wheatstone bridge, manufactured by the Clough-Brengle Co., Chicago, Ill.

Typically, the rates were determined as follows. Approximately 1–2 mg of powdered adduct was dissolved in 10 ml of solvent (at reaction temperature) and forced through a fritted glass disk filter (25–50 μ pore diameter) directly into the conductivity cell containing a further 50–75 ml of solvent and immersed in a thermostated bath at the desired temperature. After thorough shaking for *ca.* 1 min, the first point was obtained (used as zero time). Points were continuously taken until the resistance of the solution showed no change over an extended length of time (*ca.* 12 hr for erythro compounds and 24 hr for threo compounds). The value of the resistance at this time was used as the infinity point.

The first-order rate constants were determined by applying the integrated first-order rate equation

$$kt = 2.303 \log \left(\frac{\frac{1}{R_\infty} - \frac{1}{R_0}}{\frac{1}{R_\infty} - \frac{1}{R_T}} \right)$$

where t = time in seconds, R_0 = resistance at zero time, R = resistance at infinity point, and R_T = resistance at time t.

For each compound, two to seven rate determinations (each containing 30–100 data points) were made at each temperature. All calculations were accomplished by computer, using a linear least squares program containing a provision for correction of the infinity point by incremental variation. The infinity point value used was that which allowed the smallest standard deviation from the least squares line. The maximum observed correction of infinity point was 7.21%, with typical runs showing 0–1.5% correction. The linearity of each determination extended to only two or three half-lives.

The products consisted of mixtures of β-ethoxy and β-hydroxy sulfides, the relative amounts of which were determined by integration of the nmr spectra.

Two typical runs follow.

Solvolysis Products from *erythro*-3 (R = CH_3).—The mixture consisted of 86% ether and 14% alcohol: mp 73–78°; nmr ($CDCl_3$) δ 1.05–1.55 (m, 5.58, CH_3 of ether and alcohol and OCH_2CH_3), 3.25–4.00 (m, 2.72, H_2 of ether and alcohol and OCH_2CH_3), 4.54 (d, 0.86, $J_{1,2}$ = 4.9 Hz, H_1 of ether), 5.03 (d, 0.14, $J_{1,2}$ = 4.2 Hz, H_1 of alcohol), 7.16–7.50 (m, 5, aromatic protons), 7.76 (d, 0.86, $J_{1',2'}$ = 9.0 Hz, $H_{1'}$ of ether), 7.23 (d, 0.14, $J_{1',2'}$ = 9.0 Hz, $H_{1'}$, of alcohol), 8.25 (dd, 1, $J_{1',2'}$ = 9.0, $J_{2',3'}$ = 2.5 Hz, $H_{2'}$ of ether and alcohol), 8.88 (d, 1, $J_{2',3'}$ = 2.5 Hz, $H_{3'}$ of ether and alcohol).

Solvolysis Products from *threo*-3 (R = CH_3).—The mixture consisted of 84% ether and 16% alcohol: mp 101–109°; nmr δ 0.95–1.70 (m, 5.52, CH_3 of ether and alcohol and OCH_2CH_3), 2.75 (5, broad, 0.16, OH), 3.20–4.10 (m, 3, H_2 of ether and alcohol, OCH_2CH_3 and OH), 4.35 (d, 0.94, $J_{1,2}$ = 7.8 Hz, H_1 of ether), 4.85 (d, 0.16, $J_{1,2}$ = 7.2 Hz, H_1 of alcohol), 7.25–7.65

(m, 5, aromatic protons), 7.81 (d, 0.16, $J_{1',2'}$ = 9.0 Hz, $H_{1'}$ of alcohol), 7.91 (d, 0.84, $J_{1',2'}$ = 9.0 Hz, $H_{1'}$ of ether, 8.33 (dd, 1, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 2.5 Hz, $H_{2'}$ of ether and alcohol), 8.97 (d, 1, $J_{2',3'}$ = 2.5 Hz, $H_{3'}$ of ether and alcohol).

Appendix

For a nonlinear multivariable function, eq 6, the

$$f(x_k) = 0,\ k = 1, 2, 3..k \tag{6}$$

optimized values may be obtained by a numerical search technique, *i.e.*, the method of steepest descent.[47] Beginning with a good approximation to the solution, P_0, which is sufficiently close to the true solution, and proceeds along the direction of negative gradients, a point P_1 can be obtained that is closer to the true solution (eq 7)

$$P_1 = P_0 - \lambda d_0 \tag{7}$$

where $d_0 = -(\partial f/\partial x)_k$ evaluated at the base point. λ is the parameter which will minimize the function and it can be determined by a one-dimensional Fibonacci search technique, or by setting $\partial f/\partial x = 0$. This process is repeated until no further improvement is obtained.

If eq 4 is recast as eq 8, then by applying the prin-

$$J_{\text{obsd}} = \frac{(J_G + J_T e^{rE_s+C})}{(1 + e^{rE_s+C})} \tag{8}$$

ciple of least squares, eq 9 is determined.

$$\delta = \sum_i r_i^2 = \sum_i \left[J_{\text{obsd}} - \left(\frac{J_G + J_T e^{rE_s+C}}{1 + e^{rE_s+C}} \right) \right]^2 \tag{9}$$

The problem now is to find the best values that will minimize the sum of the squares of the residuals, or the function δ. The method of the steepest descent gives the following results: $J_T = 13.46$, $J_G = 2.52$, $r = 2.78$, and $C = 0.236$.

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Registry No.—**2**, 21851-47-8; *erythro*-**3**, 35031-24-4; *threo*-**3**, 35031-22-2; *erythro*-**4**, 40128-17-4; *threo*-**4**, 40128-18-5; *erythro*-**5**, 40128-19-6; *threo*-**5**, 40128-20-9; *erythro*-**6**, 40128-21-0; *threo*-**6**, 40128-22-1; *erythro*-**7**, 40128-23-2; *threo*-**7**, 40128-24-3; *erythro*-**8**, 40128-25-4; *threo*-**8**, 40128-26-5; *erythro*-**9**, 40128-27-6; *threo*-**9**, 40128-28-7; *erythro*-**10**, 40128-29-8; *threo*-**10**, 40128-30-1; *erythro*-**10'**, 40128-31-2; *threo*-**10'**, 40128-32-3; *erythro*-**11**, 40128-33-4; *threo*-**11**, 40128-34-5; *erythro*-**12**, 40128-35-6; *threo*-**12**, 40128-36-7; *erythro*-**13**, 40128-37-8; *threo*-**13**, 40128-38-9; *erythro*-**14**, 40128-39-0; *threo*-**14**, 40128-40-3; *erythro*-**15**, 40128-41-4; *threo*-**15**, 40317-80-4; *erythro*-**16**, 40128-42-5; *threo*-**16**, 40128-43-6; *erythro*-**17**, 40128-44-7; *threo*-**17**, 40128-45-8; *erythro*-**18**, 40128-46-9; *threo*-**18**, 40128-47-0; *erythro*-**19**, 40128-48-1; *threo*-**19**, 40128-49-2; *erythro*-**20**, 40128-50-5; *threo*-**20**, 40128-51-6; *erythro*-**21**, 40128-52-7; *threo*-**21**, 40128-53-8; *erythro*-**22**, 40128-54-9; *threo*-**22**, 40128-55-0; *erythro*-**23**, 40128-56-1; *threo*-**23**, 40128-57-2; *erythro*-**24**, 40128-58-3; *threo*-**24**, 40128-59-4; *erythro*-**25**, 40128-60-7; *threo*-**25**, 40128-61-8; *erythro*-**26**, 40128-62-9; *threo*-**26**, 40128-63-0; *erythro*-**27**, 40132-46-5; *threo*-**27**, 40132-47-6; *erythro*-**28**, 40132-48-7; *threo*-**28**, 40132-49-8; *erythro*-**29**, 40132-50-1; *threo*-**29**, 40132-51-2; *erythro*-**30**, 40132-52-3; *threo*-**30**, 40132-53-4; *erythro*-**31**, 40132-54-5; *threo*-**31**, 40132-55-6; *erythro*-**32**, 40132-56-7; *threo*-**32**, 40132-57-8; **34**, 528-76-7; benzyltriphenylphosphonium bromide, 1449-46-3; potassium *tert*-butoxide, 865-47-4; acetaldehyde, 75-07-0; *trans*-1-phenylpropene, 873-66-5; *cis*-1-phenylpropene, 766-90-5; propanal, 123-38-6; *cis*-1-phenyl-1-butene, 1560-09-4; *trans*-1-phenyl-1-butene, 1005-64-7; 2-methylpropanal, 78-84-2; *cis*-3-methyl-1-phenyl-1-butene, 15325-56-1; *trans*-3-butene 15325-61-8; *trans*-3,3-dimethyl-1-phenyl-1-butene, 3846-66-0; *cis*-3,3-dimethyl-1-phenyl-1-butene, 3740-05-4; 2-ethylbutanal, 97-96-1; *cis*-3-ethyl-1-phenyl-1-pentene, 40132-61-4; *trans*-3-ethyl-1-phenyl-1-pentene, 40132-62-5; 3,3-dimethylbutyltriphenylphosphonium bromide, 40139-34-2; benzaldehyde, 100-52-7; *cis*-4,4-dimethyl-1-phenyl-1-pentene, 40132-63-6; *trans*-4,4-dimethyl-1-phenyl-1-pentene, 40132-64-7; cyclopropanecarboxaldehyde, 1489-69-6; *cis*-1-cyclopropyl-2-phenylethylene, 16958-34-2; *trans*-1-cyclopropyl-2-phenylethylene, 16948-35-3; cyclobutanecarboxaldehyde, 2987-17-9; *cis*-1-cyclobutyl-2-phenylethylene, 40132-65-8; *trans*-1-cyclobutyl-2-phenylethylene, 40132-66-9; cyclopentanecarboxaldehyde, 872-53-7; *cis*-1-cyclopentyl-2-phenylethylene, 40132-67-0; *trans*-1-cyclopentyl-2-phenylethylene, 40132-68-1; cyclohexanecarboxaldehyde, 2043-61-0; *cis*-1-cyclohexyl-2-phenylethylene, 40132-69-2; *trans*-1-cyclohexyl-2-phenylethylene, 18869-27-7.

(47) G. S. Beveridge and R. S. Schechter, "Optimization: Theory and Practice," McGraw-Hill, New York, N. Y., 1970.