sured relative to the cis and corrected for the back reaction[43] and for the amount of isomerization produced by light absorbed by the piperylene ($\phi_{cis \rightarrow trans} = 0.09$).[5a] Light intensities were measured by uranyl oxalate actinometry and were typically 1.2×10^{17} photons/sec. Optimum data were obtained with piperylene isomerization of 5–15%. The ϕ_{ic} values are shown in the Results.

Emission Spectra. All solutions for fluorescence studies were degassed by bubbling with argon for 12 min; such solutions were found to be equivalent to four freeze–pump–thaw cycles at vacuum of less than 1 μ. Studies were made with *n*-hexane as solvent at 25°. Phosphorescence spectra were determined in ethanol glasses at 77°K. The cell was a 3 or 4 mm (i.d.) quartz tube attached by epoxy resin to an O-ring seal; a second O-ring seal was attached to a Kel-F high-vacuum stopcock and the two pieces joined by a Teflon O-ring. Samples were deoxygenated by four freeze–pump–thaw cycles to a vacuum of less than 1 μ. It was found that with this diameter quartz tube, relative intensities could be measured to 10–20% reproducibility.

Fluorescence Quenching by Piperylene. Solutions of the phenylacetate and varied amounts of piperylene were deoxygenated and relative fluorescence intensities determined. The data are collected in Table VIII.

Acknowledgments. We are grateful to the Public Health Service (Grant No. CA-10733, National Cancer Institute) and the National Science Foundation (Grant No. GP 7463 and GP 12650) for the generous support of this research. We also are grateful for the assistance of Professor F. Lytle in the construction and calibration of the fluorometer and P. Froehlich for obtaining some of the fluorescence quenching data.

---

[43] A. A. Lamola, Ph.D. Thesis, California Institute of Technology, Calif., 1965, p 41.

The Effect of Polar Substituents on the Barrier to Rotation about the Sulfenyl Sulfur–Nitrogen Bond in *N*-Alkyl-*N*-arenesulfonylarenesulfenamides[1,2]

Morton Raban* and Freeman B. Jones, Jr.[3]

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received August 3, 1970*

Abstract: An investigation of the effect of polar substituents on torsional barriers in *N*-isopropyl-*N*-arenesulfonylarenesulfenamides was undertaken using the methods of Hammett analysis. The results provide additional confirmation that chemical-shift nonequivalence in these compounds derives from a torsional barrier about the N–S bond. Polar substituents attached to the sulfenyl phenyl ring increase the torsional barrier. The effect of substituents in the para position is more dramatic than that of those in the meta position indicating that conjugation with the aromatic π system is important. The effect of polar substituents attached to the sulfonyl phenyl ring is quite different. When the sulfenyl phenyl ring does not have polar substituents, substitution in the sulfonyl phenyl ring has no effect on the torsional barrier. However, when the sulfenyl phenyl ring is substituted with electron-withdrawing groups, the effect of electronegative substituents in the sulfonyl phenyl ring is to lower the torsional barrier. The data are best accommodated by postulating three contributors to the sulfenamide torsional barrier: (a) overlap repulsion between nonbonding electrons on sulfur and nitrogen; (b) steric hindrance at the transition state; (c) dependence of the S–N bond strength on dihedral angle. The dihedral angle dependence of the bond strength is related to partial multiple bonding which most likely involves sulfur d orbitals.

Nuclear magnetic resonance (nmr) spectroscopy has proved to be a powerful tool for the study of the stereochemistry of trivalent nitrogen bonded to heteroatoms bearing nonbonding valence shell electrons. Compounds containing trivalent nitrogen bonded to nitrogen, oxygen, sulfur, or phosphorus have been observed to exhibit chemical-shift nonequivalence of diastereotopic substituents.[4] The coalescence of signals of diastereotopic groups has been associated with either of two conformational processes: inversion of the nitrogen pyramid or rotation about the nitrogen–heteroatom bond. Indeed, several studies have been devoted to determining which of the two, torsion or inversion, represents the slow step in the "topomerization,"[5] the conformational interchange corresponding to coalescence. In the sulfenamide system, where the heteroatom is divalent sulfur, the rate-determining step has been firmly established as rotation about the N–S formal single bond.[4a]

Among the largest torsional barriers in compounds of this type are those in sulfenamides, ranging from 12 to 20 kcal/mol. As such, sulfenamides represent useful substrates for studying the influence of structural

---

[1] Stereochemistry at Trivalent Nitrogen. XI. Part X: M. Raban and E. H. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971).

[2] (a) This work was supported in part by the National Science Foundation under Grant No. GP-17092 and by the Petroleum Research Fund, administered by the American Chemical Society, under Grant No. 1139-G. (b) Abstracted from the Ph.D. Thesis of F. B. J., Wayne State University, 1970. (c) A portion of this work has appeared in preliminary form: M. Raban and F. B. Jones Jr., *J. Amer. Chem. Soc.*, **91**, 2180 (1969).

[3] Holder of a University Fellowship at Wayne State University, 1969–1970.

[4] For leading references in this area see: (a) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 6677 (1969); (b) H. Kessler, *Angew. Chem.*, **82**, 237 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970); (c) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970).

[5] Topomerization has been suggested as a useful term to describe degenerate processes which alter the time-averaged stereochemical relationships of groups in molecules.[4b] This includes processes by which diastereotopic groups are rendered enantiotopic or equivalent on the nmr time scale. Often, as in the present instance, topomerization may be effected by degenerate racemization, the interconversion of two enantiomers in a racemic modification.

features on the magnitude of the torsional barrier. The substantial effect of steric bulk and the relative unimportance of conjugation on barriers to rotation about the sulfenamide bond have already been documented.[4a] This paper reports our findings on the effect of substituent electronegativity on the S–N torsional barrier and discusses the structural and mechanistic implications of these results. This information is necessary in order to approach an understanding of the origin of these exceptionally large torsional barriers.

Some indication that electronegativity plays a role in determining the magnitude of torsional barriers about the sulfenamide bond was present in the results of our studies on *N,N*-dialkylsulfenamides (**1**, RSNR′R″, R′ and R″ = alkyl groups).[4a] Trichloromethanesulfenamides (**1**, R = CCl_3), trifluoromethanesulfenamides (**1**, R = CF_3), and 2,4-dinitrobenzenesulfenamides (**1**, R = 2,4-dinitrophenyl) exhibited chemical-shift nonequivalence and we were able to measure torsional barriers using variable-temperature nmr spectroscopy. However, with less electronegative substituents at sulfur, *e.g.*, phenyl or *p*-tolyl, chemical-shift equivalence was observed even at temperatures as low as −70° and, hence, torsional barriers could not be measured. In order to quantitatively assess this phenomenon, however, we required a system in which torsional barriers could be measured even with other than electronegative groups at sulfenyl sulfur. The barriers could then be related to the electron-withdrawing ability of the substituent. Fortunately, in examining the nmr spectra of diastereomeric *N*-benzenesulfonylarenesulfenamides (**1**, R = aryl, R′ = $C_6H_5SO_2$, R″ = alkyl) we found that barriers could be determined even when the substituent at sulfenyl sulfur was not electronegative.[6a] We therefore chose to examine the effect of polar groups in the sulfonylsulfenamide system. Since several derivatives prepared from benzylamine exhibited accidental coincidence of signals from diastereotopic groups, we chose to carry out our study on derivatives of isopropylamine (**1**, R = aryl, R^1 = arenesulfonyl, R″ = $CH(CH_3)_2$), in which the two isopropyl methyl groups serve as a probe for chirality and degenerate racemization.[4a] In addition we were able to gain further information about the origin of the torsional barrier by examining the effect of polar substituents at the sulfonyl substituent as well.

In all, four series of compounds were examined, **2**, **3**, **4**, and **5**. In two series, **2** and **3**, we examined the effect of polar groups at the sulfenyl sulfur and in the other two, **4** and **5**, we studied the dependence of the sulfenamide torsional barrier on the electronegativity of the substituent at the other sulfur atom.

Nmr Analysis

In all cases, the rates of degenerate racemization, *i.e.*, the interconversion of enantiomers in a racemate, could be measured by observing coalescence of signals of diastereotopic methyl groups in the nmr spectrum since this degenerate racemization corresponds to a topomerization.[5] We identify the rate-determining step in the topomerization as torsion about the sulfenyl S–N bond. We may reject slow inversion at nitrogen by analogy with the *N,N*-dialkylsulfenamides in which a torsional barrier has been demonstrated.[4a] The effect of the sulfonyl group should be to lower the nitrogen inversion barrier[7] while the barriers we find in these systems are actually somewhat higher. The difference in the signs of the Hammett reaction constants for series **3** and series **5** confirms this judgement (*vide infra*). Although a torsional barrier about the sulfonyl S–N bond might be considered as a possible explanation, torsional barriers about sulfenamide bonds have been measured by nmr spectroscopy while torsional barriers in sulfonamides are apparently too low to be investigated by nmr spectroscopy unless the ligand at sulfur is highly electronegative.[6b] Nonempirical SCF–MO calculations,[8] in accord with this view, predict that the barrier to torsion in the α-mercapto carbanion (:CH_2SH) is more substantial than that in the corresponding sulfone analog (:CH_2SO_2H). Evidence confirming this conclusion may also be obtained by comparing Hammett reaction constants for series **3**, **4**, and **5** (*vide infra*).

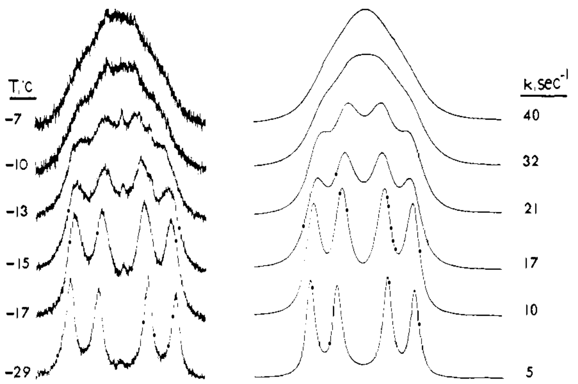


Figure 1. Experimental and theoretical spectra of *N*-benzenesulfonyl-*N*-isopropylbenzenesulfenamides **2b**, **3c**, and **4d**.

The rates and free energies of activation for degenerate racemization were evaluated using both approximate methods and by complete line-shape analysis (Table I). The approximate rates at the coalescence temperatures were calculated using eq 1. In each case, the coalescence temperature (eq 1) was

$$k_c = \pi\Delta\nu/\sqrt{2} = 2.22\Delta\nu \qquad (1)$$

assigned to the temperature at which a single broad peak was observed ($\Delta\nu > J_{AX}$) or at which two broad peaks were observed ($\Delta\nu < J_{AX}$). Strictly speaking, eq 1 does not apply to the A_3B_3X spin system observed for exchanging isopropyl methyl groups but rather is derived from the total line-shape expression for the uncoupled AB system. Nevertheless we found that the free energies obtained using this expression do not deviate significantly from those obtained by complete line-shape analysis.

The complete line-shape analysis depended on a subspectral analysis of the A_3B_3X spin system.[9] The

---

(6) (a) M. Raban, G. W. J. Kenney, Jr., J. M. Moldowan, and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **90**, 2985 (1968); (b) W. B. Jennings and R. Spratt, *Chem. Commun.*, 1418 (1970).

(7) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 357 (1967).

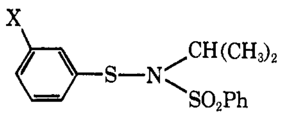
(8) (a) S. Wolfe, A. Rauk, and I. G. Csizmadia, *ibid.*, **91**, 1567 1969); (b) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *Chem. Commun.*, 96 (1970).

(9) This approach was suggested by: S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, **40**, 1189 (1964).

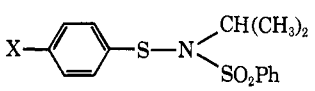
Table I. Nmr Parameters and Free Energies of Activation for Degenerate Racemization

Compd	σ^a	$\Delta\nu$, Hz[b]	k_{app}[c]	k_{clsa}[d]	T_c, °C	$\Delta G_{app}^{\ddagger}$[c]	$\Delta G_{clsa}^{\ddagger}$[d]
2a	−0.07	17.4	38	39	−8.5	13.5	13.5
2b	0.0	18.2	40	40	−7	13.6	13.6
2c	0.23	17.4	38	39	4	14.2	14.2
2d	0.78	17.5	38	40	−10	14.5	14.5
3a	−0.27	18.5	41	41	−14	13.2	13.2
3b	−0.17	19.0	42	42	−18	13.0	13.0
3c	0.00	18.2	40	40	−7	13.6	13.6
3d	0.23	18.7	41	42	5	14.2	14.2
3e	0.78	19.2	42	42	35	15.8	15.8
4a	−0.17	16.7	37	38	−11	13.4	13.4
4b	0.00	18.2	40	40	−7	13.6	13.6
4c	0.23	17.2	38	39	−16.5	13.3	13.3
4d	0.78	15.4	24	36	−10.5	13.4	13.3
5a	−0.17	18.4	41	41	115	20.1	20.1
5b	0.00	21.0	47	46	111	19.7	19.7
5c	0.23	20.8	46	46	107	19.5	19.5
5d	0.78	21.5	48	47	95	18.9	18.9
6a[e]	1.58[f]	7.0	16	20	73	18.4	18.2

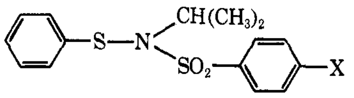
[a] Taken from ref 10. [b] All spectra taken in *ca.* 10% toluene-d_8 except as indicated. [c] First-order rate constant in sec^{-1} calculated using eq 1. Free energy of activation in kilocalories per mole obtained using the Eyring equation. [d] First-order rate constant in sec^{-1} obtained by complete line-shape analysis. Free energy of activation in kilocalories per mole obtained using the Eyring equation. [e] Shows chemical-shift equivalence in toluene-d_8, nonequivalence in bromobenzene and nitrobenzene. [f] Sum of ortho and para substituent constants.



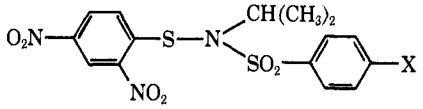
2a, X = CH_3
b, X = H
c, X = Cl
d, X = NO_2



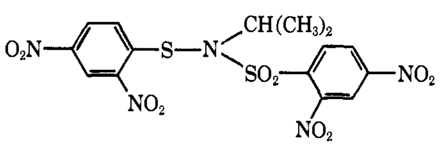
3a, X = OCH_3
b, X = CH_3
c, X = H
d, X = Cl
e, X = NO_2



4a, X = CH_3
b, X = H
c, X = Cl
d, X = NO_2



5a, X = CH_3
b, X = H
c, X = Cl
d, X = NO_2



6a

four-line A_3B_3 portion of the spectrum was divided into two uncoupled AB subspectra, one corresponding to an α spin for H_X and the other, shifted upfield by J_{AX}, corresponding to a β spin for H_X. Spin transitions involving H_X cannot occur at a rate comparable to the topomerization, since the chemical shift of H_X is far removed from the region of the spectrum being irradiated. Consequently, molecules in the two different H_X spin states undergo topomerization as independently as if they were different chemical species. The line shape for the methyl region of the exchanging isopropyl group was simulated by two separate pairs of peaks, each corresponding to an uncoupled AB spin system, using a computer program CLASS based on the solution of the exchange-modified Bloch equations. The two pairs were chemically shifted by 6.5 Hz, the experimentally measured methyl–methine coupling constant. The intensity of the upfield pair of singlets was scaled to 90% of the intensity of the downfield pair corresponding to the experimentally observed second-order perturbation in the nearly first-order spectrum. In all cases identical rates of exchange, chemical-shift differences, and relaxation times were used for the two subspectra. The shapes of the theoretical spectra closely approximated those obtained experimentally (Figure 1) confirming that the assumptions made in the spectral simulation are valid. Although it is possible, in principle, to obtain Arrhenius activation energies by matching experimental and theoretical spectra, substantial errors are often encountered if the temperature range is small, *i.e.*, unless the chemical-shift difference is large. For purposes of analyzing the effect of electronegativity on the torsional barrier we used the free energy of activation rather than the Arrhenius activation energy or the enthalpy of activation since the former can be determined with greater precision and consequently is the more meaningful parameter for analysis.[4b]

The complete line-shape analysis program was used to prepare a plot of k_c as a function of the chemical-shift difference for the system in which the chemical shift exceeded the methyl–methine coupling constant, using the experimental values of T_2 and J_{AX}, which were essentially constant for the compounds investigated. A straight line was obtained by linear least-squares analysis which obeyed the analytical expression 2. The validity of this expression was checked by simulation of spectra and matching with experimental spectra for several interpolated points. We were gratified to observe that the free energies of activation determined by complete line-shape analysis were in close agreement with those obtained by the use of the approximate

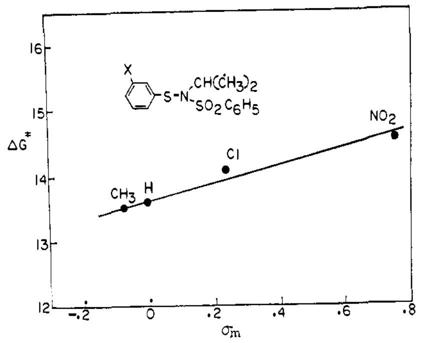


Figure 2. Hammett plot for series **2**.

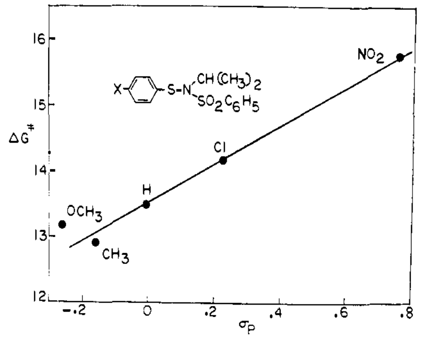


Figure 3. Hammett plot for series **3**.

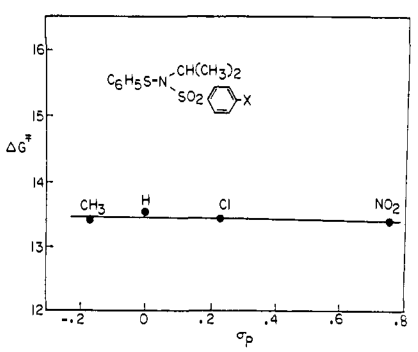


Figure 4. Hammett plot for series **4**.

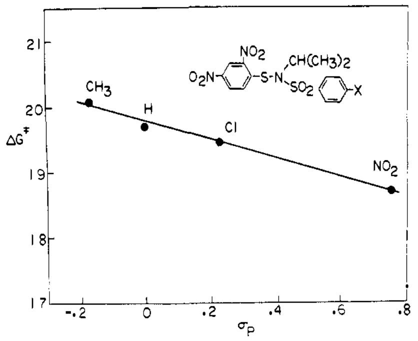


Figure 5. Hammett plot for series **5**.

eq 1. We may conclude from this that free energies of activation for exchange of diastereotopic isopropyl methyl groups determined in the past using this approximate equation are probably reliable. The data obtained are listed in Table I.

$$k_c = 1.69\Delta\nu + 10.6 \qquad (2)$$

Hammett Analysis

The methods involving linear free-energy relationships, which have come to be known as Hammett analysis,[10] were used to assess the importance of polar substituents on the torsional barrier. The normal rate constant form of the Hammett equation (eq 3), where k_{ij} is the rate in the jth system with the ith substituent, is not convenient for analysis of the barriers obtained by coalescence of signals from diastereotopic groups since the most reliable parameter obtained is the free energy of activation, and each value corresponds to a different temperature. Consequently, we modified the free-energy form of the Hammett equation (eq 4). Since the temperature is not constant, we replace $T\rho_j$ by ρ_j' to give eq 5. This approach furnishes a reaction constant, ρ', which is independent of temperature in contrast to the usual Hammett reaction constant, ρ, which might be expected to exhibit an inverse proportionality to temperature for reactions with negligible entropies of activation.[10] We note that this approach requires that free energies of activation be temperature independent or nearly so over the range of measurement, a restriction which is obeyed for the system at hand. For purposes of comparison with Hammett reaction constants in the literature, we also calculated a hypothetical ρ corresponding to a temperature of 300°K, $\rho_{300} = \rho'/300$.

$$\log (k_{ij}/k_{oj}) = \rho_j\sigma_i \qquad (3)$$

$$\Delta G_{ij}^{\ddagger} = 2.3RT\rho_j\sigma_i + \Delta G_{oj}^{\ddagger} \qquad (4)$$

$$\Delta G_{ij}^{\ddagger} = 2.3R\rho_j'\sigma_i + \Delta G_{oj}^{\ddagger} \qquad (5)$$

Using the methods above and substituent constants from the literature (σ_m for **2** and σ_p for **3**, **4**, and **5**) the free energies of activation were fitted to eq 5 using linear least-squares analysis (Figures 2–5, Table II).

Table II. Hammett Correlations of Free Energies of Activation

Series	Hammett constants	$\rho^{b,c}$	$\rho_{300}{}'^{c,d}$	r^e
2	σ_m	-282 ± 20	-0.9 ± 0.1	0.963
3	σ_p	-582 ± 55	-1.9 ± 0.2	0.986
3[a]	σ_p	-638 ± 15	-2.1 ± 0.1	0.999
4	σ_p	11 ± 25	0.0 ± 0.1	−0.300
5	σ_p	246 ± 17	-0.88 ± 0.1	−0.996
5[f]	σ_p	198 ± 23	0.66 ± 0.1	−0.978

[a] Excluding data for **3a**. [b] ρ determined by linear least-squares correlation. [c] Error ranges are standard deviations. [d] Calculated Hammett reaction constant at 27°. [e] Correlation coefficient. [f] Including the data for **6**. The substituent constant used was obtained by summing ortho and para constants.

Two separate correlations were made for **3**, one including and one excluding the point for **2a** (R = OCH_3), the one point most out of line. As the data in Table II indicate, the slope is not markedly changed by the exclusion of this point although the correlation coefficient is slightly improved. The deviation of methoxy compounds from linear free-energy correlations is a well-known phenomenon. Similarly two correlations were

---

[10] (a) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, Chapter 11; (b) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); (c) H. H. Jaffe, *ibid.*, **53**, 191 (1953); (d) O. Exner, *Collect. Czech. Chem. Commun.*, **31**, 65 (1966).

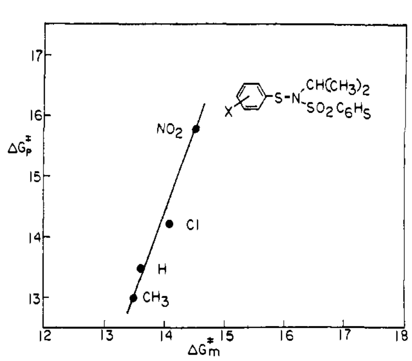


Figure 6. Free energies of activation for compounds with para substituents as a function of those for compounds with the same substituent in the meta position (Exner plot).

made for **5**, one including and one deleting the data for **6**. Again the inclusion has little effect on the reaction constant but results in a decrease in the correlation coefficient. The inclusion of ortho substituents, in general, leads to deviations from linearity when the reaction at hand has steric components, as in the present instance.

Although the reaction constants for series **2** and **3** should be the same, the analyses resulted in a significant difference. This phenomenon, the greater sensitivity of the barrier to para substituents as compared with meta substituents, can be quantitatively represented by the Exner plot[10a,d] (Figure 6) of free energies of compounds in series **2** as a function of those for compounds in series **3** with the same substituent ($\Delta G_p^{\ddagger}$ *vs.* $\Delta G_m^{\ddagger}$). The slope obtained for this plot, 4.5, is much higher than the corresponding slope obtained by Exner for the dissociation of benzoic acid, 1.14.[10d] The slope obtained by Exner represents K_I, the ratio of para to meta substituent constants, which should obtain when inductive effects only are important. The deviation, therefore, represents an important contribution of "through-resonance"[10a] to the effect of polar substituents on the torsional barrier. Using the reaction constant obtained for meta substituents, ρ_m', series **2**, a new set of para substituent constants σ_s was calculated using expression 6 (Table III). The values of σ_s obtained are more similar to σ^- values in the literature than to σ_p

$$\sigma_s = \frac{\Delta G^{\ddagger} - \Delta G_o^{\ddagger}}{2.3R\rho_m'} \qquad (6)$$

values, indicating that an important part of the polar substituent effect involves conjugation of the aromatic π system with an orbital on sulfur.

Table III. Comparison of σ_s Values with Other Hammett σ Values

R	$\Delta G_p^{\ddagger}$	$\Delta G_p^{\ddagger} - \Delta G_o^{\ddagger}$ [a]	σ_s[a]	σ_m	σ_p	σ^- [b]
OCH$_3$	13.15	−0.45	−0.31	0.12	−0.27	−0.2
CH$_3$	12.95	−0.65	−0.46	−0.07	−0.17	−0.31[c]
H	13.55	−0.05	0.00	0.00	0.00	0.00
Cl	14.18	0.58	0.48	0.37	0.23	0.11[c]
NO$_2$	15.76	2.16	1.71	0.71	0.78	1.24

[a] Values taken from expression $\Delta G_p^{\ddagger} = -2.3R\rho_m'\sigma_s + \Delta G_o^{\ddagger}$. $\Delta G_p^{\ddagger}$ are free energies of activation for compounds with para substituents, **3**; $\Delta G_o^{\ddagger}$ and ρ_m' were determined from the Hammett plot of activation free energies for compounds with meta substituents, **2**. [b] Taken from ref 10. [c] σ^+ values.

The reaction constants obtained for substituents on the sulfonyl phenyl ring are conspicuously different from those obtained for series **2** and **3**. That for **4** is 0 and that for **5** is opposite in sign. These results confirm our suggestion that the process under observation is torsion about the sulfenyl S–N bond. If nitrogen inversion were the slow step in the topomerization the reaction constants for both rings should be of the same sign. Although different magnitudes might be expected, it does not seem probable that differences in the transmitting ability of the sulfenyl and sulfonyl sulfur linkages would result in a complete inversion in direction for the effect of polar substituents.

The relative magnitudes of the effects in series **3** and **5** rule out torsion about the sulfonyl S–N bond as the rate-determining step.[6b] If the sulfonyl sulfur atom were directly involved we would surely expect the substituent constants for **4** and **5** to be greater than that of **3**. Further, the large difference between the dependencies on substituent electronegativity for **4** and **5** indicates that substituents on the sulfonyl ring affect the barrier only insofar as substitution here opposes the effect of electron-withdrawing groups attached to the sulfenyl ring.

Discussion

Barriers to nitrogen inversion as well as to rotation in compounds with nitrogen–heteroatom bonds have been attributed, at least in part, to lone pair–lone pair interaction in the transition states for topomerization. Increased overlap between the filled lone-pair orbitals is expected to result in repulsion (an increase in total energy) rather than the stabilization which would occur were there only two electrons present in the two orbitals. One may view this by noting that overlap leads to the creation of bonding and antibonding molecular orbitals. Since there are four electrons, both bonding and antibonding levels are fully occupied and a net destabilization occurs from electron correlation.

Naively, one might predict that electronegative substituents attached to the heteroatom would decrease lone pair–lone pair repulsions and lower torsional barriers about nitrogen–heteroatom bonds. The Hammett reaction constants for **2** and **3** indicate that this is decidedly not the case for sulfenamides. Electron-withdrawing substituents at the sulfenyl sulfur atom markedly increase the torsional barrier. This result implies that another contributor to the torsional barrier should be considered in addition to lone pair–lone pair repulsions and steric hindrance. One hypothesis which can accommodate the experimental findings involves partial S–N double bonding involving the nitrogen lone pair orbital and an orbital on sulfur. Further, we must postulate that the bond strength must be a function of the S–N dihedral angle in order for partial double bonding to result in a torsional barrier. The inversion of sign of the Hammett reaction constant upon going from series **3** to series **5** is readily understood in terms of this hypothesis. When the electronegativity of the sulfonyl phenyl ring is increased, the sulfonyl sulfur atom is able to compete with the sulfenyl sulfur atom in partial double bonding with the nitrogen lone pair orbital. The bond order of the sulfenyl S–N bond is reduced, as is the torsional barrier. The independence of the torsional barrier in **4** with respect to substituents in the para position of the sulfonyl phenyl ring then must indicate that partial double bonding in the sulfenyl S–N bond makes a negligible contribution to the barriers in this series. Only when a strongly electronegative group is attached to sulfenyl sulfur is partial double bonding important enough to make a substantial contribution to the barrier. Consequently, we regard the barriers in series **4** as deriving mainly from electron repulsion and steric hindrance.

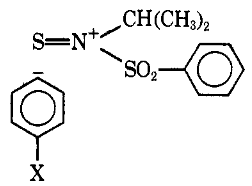
If a measure of the contribution of steric factors to the barriers in series **4** could be obtained, it would be possible to estimate the contribution of electron repulsion to the barrier. The effect of increasing the size of a ligand at nitrogen from methyl to secondary or tertiary alkyl in an *N*-dialkylsulfenamide is to increase the torsional barrier by 2 kcal/mol for a secondary group or 4 kcal/mol for a tertiary substituent. On this basis, steric factors in series **4** contribute, at least on the order of 5–6 kcal/mol, since a secondary group is present and the arylsulfonyl group may be expected to approach the bulk of a *tert*-alkyl group. Thus, the contribution of lone pair–lone pair repulsion is likely to be on the order of 7 kcal/mol, the difference obtained when the steric contribution is subtracted from the total barriers in series **4**.

The difference between the highest barrier observed in series **5** and the barriers in series **4** represents the maximum contribution of partial double bonding to the barrier, *viz.* 7 kcal/mol. This need not represent the bond strength of the partial double bond but it may be regarded as a minimum value. If the partial double bond is not completely broken at the torsional transition state the bond strength must actually be somewhat higher. On this basis it would appear that the creation of partial multiple bonding in the S–N bonds makes a contribution to the barriers in series **5** which is at least as important as repulsion between pairs of nonbonded valence electrons.

The result of a recent X-ray crystallographic structure determination of a representative *N*-alkylsulfenylsulfonamide provides evidence supporting the existence of partial double bonding involving the nitrogen lone pair.[11] The geometry of substitution at nitrogen in the derivative is nearly planar. The sum of bond angles at the nitrogen is 356° compared to the 360° which would be obtained were nitrogen completely planar. The preference for sp^2 hybridization at nitrogen implies the existence of π bonding which is facilitated by increased p character in the nitrogen lone-pair orbital.

Two possibilities may be considered in specifying the orbital on sulfur involved in bonding with the nitrogen lone pair. The most obvious choice would seem to be one of the empty sulfur d orbitals. There are two immediate objections to such a choice, however: the considerably higher energy of the d orbitals on sulfur with respect to the lone-pair orbital on nitrogen, and the multiple degeneracy of the d orbitals. Since sulfur d orbitals are high in energy, overlap with orbitals in the second shell may be expected to be poor. In geometrical terms this is often expressed by drawing attention to the diffuseness and greater size of the 3d orbitals. In accord with this view, involvement of sulfur d orbitals makes a negligible contribution to torsional barriers about the sulfur–carbanion bonds in *ab initio* SCF–MO calculations.[6] However, it is possible that the presence of an electronegative substituent at sulfenyl sulfur may result in a contraction of the d orbitals and lower their energy until overlap with the nitrogen lone-pair orbital is substantial and leads to significant stabilization. The negative Hammett reaction constants found for series **2** and **3** are readily understandable in terms of this hypothesis.

Even if substantial p–d π bonding were to exist, this would not of necessity lead to a torsional barrier. The creation of a torsional barrier requires a dependence of bond strength on the S–N dihedral angle. Indeed, it has been assumed that the dihedral angle requirement for p–d π bonding must be small since the multiple degeneracy of d orbitals would allow overlap with one of the d orbitals at any dihedral angle.[12] However, Cowley, *et al.*,[4c] have argued that mixing of d orbitals with σ bonding orbitals can remove degeneracy and lead to torsional barriers. Further, orbitals should be completely degenerate only in spherical atoms and any unsymmetrical substitution will lead to the creation of a ligand field which will result in splitting of d orbitals. This splitting may be expected to be greater when conjugation with only a particular d orbital is possible, as in the present instance. In a sense one of the sulfur d orbitals acts to transmit the effect of polar substituents to the nitrogen lone pair by being able to overlap with both the aromatic π system and the lone pair orbital on nitrogen in the torsional ground state but not in the transition state for torsion.



7

A second possibility involves negative hyperconjugation which may be expressed by canonical form **7**. We can also describe this kind of bonding in molecular orbital terms as overlap between the nitrogen lone pair orbital and the σ^* orbital corresponding to the *S*-aryl σ bond. Alternatively, we might imagine that the linear combination of the nitrogen lone-pair orbital and orbitals on sulfur and carbon would result in three molecular orbitals, two of which are bonding and one that is antibonding. This overlap expressed in either of these three ways is possible only in the torsional ground state when the CSN plane bisects the angle formed by the two other ligands at nitrogen.

Examination of the results of Hammett analysis of series **2** and **3** offers tentative evidence pertinent to distinguishing between these two possibilities. Thus, if a σ orbital, which is not in direct conjugation with the aromatic π system, is involved we would expect inductive withdrawal of electron density to be of paramount importance. On the other hand, contraction of the 3d orbitals would involve substantial importance of resonance. The Exner plot of free energies in series **3** as a function of those in series **2** had a slope of 4.5. If in-

---

(11) J. Kay, M. Glick, and M. Raban, *J. Amer. Chem. Soc.*, in press.

(12) W. von E. Doering and L. K. Levy, *J. Amer. Chem. Soc.*, 77, 509 (1955); W. von E. Doering and A. K. Hoffmann, *ibid.*, 77, 521 (1955); M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

Table IV. Physical Properties and Analytical Data[a]

			Anal.					
			Calcd, %			Found, %		
Compd	Mp, °C	Yield, %	C	H	N	C	H	N
2a	60–63	79	59.81	4.92	4.36	59.99	4.93	4.30
2b	92–94	54	58.63	4.53	4.56	58.73	5.25	4.29
2c	72–73.5	80	52.78	4.69	4.10	52.42	4.89	4.12
2d	116–118[b]	71	50.99	4.53	7.93	50.71	4.61	7.99
3a	122–125	49	57.00	5.46	4.17	56.82	5.35	3.91
3b	118–120	50	59.81	4.92	4.36	60.00	4.97	4.26
3d	125–127	50	52.78	4.69	4.12	52.98	4.71	4.03
3e	119–121[b]	23	50.99	4.53	7.93	50.70	4.35	7.93
4a	104–107	37	59.81	4.92		60.05	4.73	
4c	75–78	32	52.78	4.69	4.12	52.51	4.73	4.28
4d	129–131[b]	27	51.14	4.10		51.45	4.73	
5a	116–117[b]	47	46.71	4.14	10.21	46.94	3.90	10.45
5b	154–157[b]	38	45.22	4.02	10.55	44.25	3.93	10.84
5c	112–114[b]	32	35.45	3.53	10.60	45.20	3.80	10.52
5d	176–178[b]	24	40.72	3.17	12.67	40.94	3.41	12.92
6a	206–208[b]	50	39.56	2.85	15.38	39.77	2.65	15.21

[a] All compounds were colorless crystalline solids except as indicated. [b] Yellow crystals.

ductive effects only were involved, a slope of 1.14 would be expected. Clearly, resonance plays a predominant role in mediating the effect of polar groups. The similarity of the calculated σ_S to values for σ^- also suggests interaction with 3d orbitals is important. The conclusions of other authors[4c,6b] that p-d π bonding can result in torsional barriers are in accord with this view.

Experimental Section

Variable-temperature nuclear magnetic resonance spectra were measured on a Varian A60-A spectrometer. Chemical shifts are reported in parts per million on the δ scale and refer to 10–20% solution (w/v). Chemical-shift differences between diastereotopic protons are reported in hertz. Temperatures were calibrated with methanol or ethylene glycol spectra as described in the Varian users manual. Each coalescence temperature was measured three times and the results were averaged. In general, duplicate measurements were within ±2°. Melting points were measured on a Thomas-Hoover melting point apparatus. Elemental analyses were performed by Midwest Microlab, Inc. Infrared spectra were taken with a Perkin-Elmer 137 spectrophotometer.

Theoretical spectra were generated by an IBM 360/65 computer and plotted on a Calcomp plotter using a program CLASS based on the solution to the exchange-modified Bloch equations. The rate at coalescence (k_c) was assigned in either of two ways: (1) as the lowest rate at which the minimum between two resonances disappeared, *i.e.*, became a saddle point or maximum, and (2) as the lowest rate at which a broad singlet occurs. Plots of k_c as a function of $\Delta\nu$ were constructed from which k_c could be determined for intermediate values of $\Delta\nu$. The analytical expressions obtained with linear least-squares standard deviations were: (1) $k_c = (2.40 \pm 0.00)\Delta\nu + (12.0 \pm 0.0)$; (2) $k_c = (1.69 \pm 0.05)\Delta\nu + (10.6 \pm 0.9)$. The correlation coefficients were 1.000 and 0.996, respectively. The values obtained using both definitions were in agreement. The value of T_2 chosen was based on the observed width at half-height at the slow exchange limit, and tetramethylsilane was used as a standard for magnetic inhomogeneity as well as chemical shift.

Arenesulfenyl Chlorides. Arenesulfenyl chlorides, except as indicated, were prepared from the corresponding thiols.[13] A solution of the arene thiol in 50 ml of CCl_4 was added dropwise over a period of 1 hr to a cold solution of chlorine (10 g/0.06 mol of thiol) in 300 ml of anhydrous CCl_4 in which one or two crystals of iodine had been dissolved. After an additional 30 min of stirring, the solvent and excess chlorine were rapidly removed *in vacuo*, leaving the crude sulfenyl chloride as an orange-red mobile liquid. The rate of the reaction was followed by monitoring the disappearance of the S–H bond at *ca.* 4.0 μ in the ir spectrum. Rapid distillation under reduced pressure afforded the pure sulfenyl chloride. The pure sulfenyl chlorides were stored under nitrogen at 15°: benzenesulfenyl chloride, bp 55° (1 mm) (lit.[14] bp 77.5–78.5° (2.5 mm)); *p*-methoxybenzenesulfenyl chloride, bp 70–72° (0.3 mm) (lit.[14] bp 128–130° (17 mm)); *p*-chlorobenzenesulfenyl chloride, bp 68–69° (0.5 mm) (lit.[14] bp 94° (6 mm)); *m*-toluenesulfenyl chloride, bp 90–91° (0.1 mm).

Nitrobenzenesulfenyl Chlorides.[15] A stream of chlorine, dried by bubbling through concentrated sulfuric acid, was added to a suspension of 30 g (0.1 mol) of 3,3- or 4,4-dinitrodiphenyl disulfide in 200 ml of dry carbon tetrachloride. The rate of flow of chlorine was regulated so that 10 g reacted over a period of 2–2.5 hr at a temperature maintained at 50–60°. The solid dinitrodiphenyl disulfide gradually disappeared and at the end of the reaction time a dark yellow solution was obtained. The warm solution was filtered through a hot Buchner funnel. The excess chlorine and the solvent were rapidly removed *in vacuo*, leaving an orange-red liquid. Rapid distillation under reduced pressure afforded *m*-nitrobenzenesulfenyl chloride, bp 120° (1.0 mm) (lit.[14] 140° (5 mm)). *p*-Nitrobenzenesulfenyl chloride was recrystallized from carbon tetrachloride, mp 50–52° (lit.[14] mp 52°). 2,4-Dinitrobenzenesulfenyl chloride was obtained commercially.

***m*-Chlorobenzenesulfenyl Chloride.** *m*-Chlorobenzenethiol was prepared according to the general method of Schellenberg and Westheimer.[16] A solution of 7.2 g of sodium nitrite in 20 ml of water was added at −2° over a period of 15 min to a stirred solution containing 25.6 g (0.2 mol) of *m*-chloroaniline, 22 ml of concentrated hydrochloric acid, and 150 ml of water. After stirring the diazotized solution for an additional 30 min, the excess nitrite was destroyed by dropwise addition of a saturated solution of urea. This suspension was added over a period of 30 min to a stirred solution of potassium ethyl xanthate in 100 ml of water. After the addition, the solution was heated at 80° for 30 min, cooled to 5°, extracted with ether, and washed with water. The ether was removed *in vacuo* and the aryl ethyl xanthate saponified by refluxing with 200 ml of ethanol and 20 g of potassium hydroxide under nitrogen for 16 hr. The mixture was extracted with ether, washed with acid and water, and extracted into 1 *N* sodium hydroxide. The alkaline extract was acidified and reextracted with ether and dried over magnesium sulfate. The ether was removed *in vacuo*. The material was identified by the principal ir S–H band at 3.95 μ. This mercaptan was converted directly into the sulfenyl chloride (*vide supra*), bp 90° (2 mm) (lit.[14] 118° (21 mm)).

***N*-Isopropylarenesulfonamides.**[17] A solution of 0.1 mol of the sulfonyl chloride in benzene (50 ml) was added dropwise to a solution of 0.2 mol of isopropylamine in benzene (150 ml). When the addition was complete the solution was refluxed for 1 hr. Upon cooling the reaction mixture was washed with water and dried

---

[13] F. Kurzer and J. R. Powell, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 934.

[14] F. Montanari, *Gazz. Chim. Ital.*, **86**, 406 (1956); *Chem. Abstr.*, **52**, 8999h (1958).

[15] M. H. Hubacher, "Organic Syntheses," Collect. Vol II, Wiley, New York, N. Y., 1943, p 455.

[16] K. A. Schellenberg and F. H. Westheimer, *J. Org. Chem.*, **30**, 1859 (1965).

[17] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1959.

over magnesium sulfate and the anhydrous benzene solution was filtered. Crystalline sulfonamides were obtained by concentrating and cooling the benzene solution in an ice bath. The crystals which formed were recrystallized from ethanol. The liquid sulfonamide was distilled *in vacuo* after evaporation of solvent: *N*-isopropylbenzenesulfonamide, mp 101–102° (lit.[18] mp 101.5°); *N*-isopropylbenzenesulfonamide, bp 162–164° (4 mm) (lit.[19] bp 190° (13 mm)); *N*-isopropyl-*p*-toluenesulfonamide, mp 48–50° (lit.[20] mp 49–50°); *N*-isopropyl-*p*-chlorobenzenesulfonamide, mp 84–86° (lit.[21] mp 85–86°); *N*-isopropyl-*p*-nitrobenzenesulfonamide, mp 114–116° (lit.[22] mp 114–115°); *N*-isopropyl-2,4-dinitrobenzenesulfonamide, mp 98–100°.

***N*-Isopropyl-*N*-arenesulfonylarenesulfenamides 2–6.** Butyllithium (2.8 ml of a 23% solution in hexane) was added dropwise over a period of 30 min to a well-stirred solution of 0.01 mol of the appropriate sulfonamide in 75 ml of anhydrous benzene under nitrogen. A precipitate of the lithium salt formed after about 15 min. After stirring for an additional 30 min, a solution of the appropriate sulfenyl chloride (0.01 mol) in 25 ml of dry benzene was added. The reaction mixture was stirred at room temperature for a minimum of 3 hr and then filtered. The reaction mixture can be tested for completion with starch–iodide paper. A negative test signifies completion and indicates that there is no sulfenyl chloride present. The filtrate was successively washed with water, 10% sulfuric acid, 10% sodium bicarbonate, and water, dried over anhydrous magnesium sulfate, and concentrated to *ca.* 50 ml *in vacuo*. The concentrate was cooled and the precipitate recrystallized from ethanol. Care must be taken with some of the more sensitive compounds, *e.g.*, 2,4-dinitrobenzenesulfenyl derivatives, because alcoholysis may take place at high temperatures or upon prolonged heating. Physical properties and analytical data are given in Table IV.

(18) A. Nickon and A. S. Hill, *J. Amer. Chem. Soc.*, **86**, 1152 (1964).
(19) J. v. Braun, F. Jostes, and A. Wagner, *Ber. Deut. Chem. Ges. B*, **61**, 1423 (1928).
(20) M. Sekiya and K. Oishi, *J. Pharm. Soc. Jap.*, **73**, 1017 (1953); *Chem. Abstr.*, **48**, 10663f (1954).
(21) M. Kulka, *J. Amer. Chem. Soc.*, **72**, 1215 (1950).
(22) K. N. Campbell, B. K. Campbell, and E. M. Salm, *Proc. Indiana Acad. Sci.*, **57**, 97 (1948); *Chem. Abstr.*, **43**, 4630c (1949).

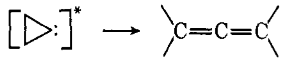
Reactions of Metastable Singlet Carbon Atoms with Unsaturated Hydrocarbons

P. S. Skell,* J. E. Villaume,[1] J. H. Plonka,[2] and F. A. Fagone

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802.
Received April 3, 1970

Abstract: Carbon atoms produced in a low-intensity carbon arc under high vacuum react with olefins on their cocondensation at a liquid nitrogen cooled surface to give dienes as well as the allenes previously reported. The diene forming reaction is assigned a singlet precursor and occurs by insertion into allylic carbon–hydrogen bonds followed by hydrogen migration; the stereochemistry of the original olefinic site is essentially retained. Previous work concerning atom plus olefin systems is reevaluated in light of the present results.

Previous work using carbon atoms aged in neopentane matrices suggested[3] that the metastable ^{1}S state was the species responsible for allene formation from olefins. Similar behavior was observed in the reaction of recoil carbon-11 with ethylene[4] where metastable, singlet atoms were designated as the species responsible for allene formation. In both cases it was postulated



that the exothermic production of a singlet cyclopropylidene was accompanied by rapid collapse to an allene. This description of the carbon plus olefin reaction is consistent with recent theoretical results[5] which also require a ^{1}S carbon atom for allene formation. The photolysis of carbon suboxide at 3000 Å with olefins[6] gave allenes from a conversion of cyclopropylideneketene to a hot cyclopropylidene. Recoil ^{11}C is also known to react with olefinic substrates by carbon–hydrogen bond insertion as well as by the carbon–carbon double bond insertion pathways.[7,8] We now report that the metastable singlet carbon atoms also react with olefins by a carbon–hydrogen insertion mechanism which leads to diene formation.

Results and Discussion

A. Ethylene. The cocondensation of carbon vapor and ethylene at a liquid nitrogen cooled surface yields allene and propyne as the major ethylene plus carbon atom (1:1) products. An ambiguity exists in this result since excited-state C_3 molecules are known to react with alcohols to give allene and propyne[9] and similar reactions may be occurring in the ethylene system. To determine the relative importance of the C_1 and C_3 pathways to allene and propyne, an ethylene reaction with carbon-14 enriched carbon vapor was carried out. Table I gives the yields of allene and propyne and their molar activities relative to 1-pentyne, which is assigned a C_3 precursor in this system ($C_2H_4 + C_3 \rightarrow HC{\equiv}CCH_2CH_2CH_3$)[10] and therefore must have

---

(1) NASA Trainee, 1967–1970.
(2) NIH Predoctoral Fellow, 1967–1970.
(3) P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **89**, 2912 (1967).
(4) M. Marshall, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4741 (1964).
(5) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *ibid.*, **92**, 3505 (1970).
(6) C. Willis and K. D. Bayes, *ibid.*, **88**, 3203 (1966); D. G. Williamson and K. D. Bayes, *ibid.*, **90**, 1957 (1968).
(7) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 201 (1964).
(8) C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965).
(9) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **91**, 699 (1969).
(10) The bisethanoallenes are usually the C_3 products from olefins; however, the parent bisethanoallene does not have sufficient stability to allow isolation although infrared examination of the crude reaction