thermostat and an excess of methyl, ethyl, or 2-propyl iodide (see Results and Discussion section) was added dropwise. The mixture was stirred at 0 °C for 2 h and then poured on water and extracted with ether. The ether was washed with water, dried, and evaporated. The reaction mixture was analyzed by GLC, TLC, and NMR, and the reaction products were isolated and purified by column chromatography on silica gel with light petroleum as eluant.

The results of the reactions carried out according to this procedure are described in the Results and Discussion section. The physical and NMR data of the products **13**, **22**, **27**, **29**, **31**, and **32**, obtained in this way, are reported above. These compounds were also obtained, with similar yields, starting from the β-bromostyrenes and the di-, tri-, and tetrachloroethylenes by reaction with MeSNa or Me_2CHSNa and then with sodium. Reaction conditions were identical with those described above for the vinylic substitutions and for the dealkylations of the vinyl alkyl sulfides with sodium.

Single-Crystal X-ray Work. Crystals of compounds **14** and **15** were mounted on a Philips PW 1100 automatic diffractometer, equipped with graphite monochromatized Mo Kα radiation. Compound **14** resulted to be monoclinic, space group $P2_1/n$ (from systematic extinctions), with lattice parameters $a = 11.150$ (3) Å, $b = 10.294$ (3) Å, $c = 5.216$ (3) Å, $\beta = 91.54$ (2)°. Assuming two molecules in the cell, the calculated density is 1.332 g·cm^{-3}, in agreement with the empirical value of 1.30 g·cm^{-3}, which can be computed according to the method of Immirzi and Perini.[35] Since the multiplicity of the general position in the space group is four, the molecule must lie on the inversion center, i.e., it must have the *E* configuration. Further structural work was deemed unnecessary.

Crystals of compound **15** are orthorhombic, acentric, space group $Pca2_1$, with cell constants $a = 9.429$ (3) Å, $b = 5.928$ (3) Å, $c = 13.848$ (3) Å; the calculated density is 1.578 g·cm^{-3} for four molecules in the unit cell, in agreement with the experimental value of 1.55 g·cm^{-3} obtained by flotation method. The intensity data of 503 independent reflections were measured; 377 of these, having $I \geq 3\sigma(I)$, were considered as "observed" and used in subsequent calculations. After the usual corrections, the structure was solved by direct multisolution method with the program MULTAN[36] and refined isotropically by the least-squares method to an *R* value of 0.14. The structural work was ended at this stage; the molecule in the solid state has the *E* configuration.

Acknowledgment. Financial support from the CNR, Rome, is gratefully acknowledged. We thank Prof. P. F. Zanazzi, Istituto di Mineralogia, University of Perugia, for his kind cooperation in carrying out the X-ray work.

Registry No. **1**, 588-72-7; **2**, 87373-88-4; **3**, 15436-06-3; **4**, 71338-94-8; **5**, 15436-11-0; **6**, 588-73-8; **7**, 80806-45-7; **8**, 35822-50-5; **9**, 87373-89-5; **10**, 37630-43-6; **11**, 156-60-5; **12**, 40588-88-3; **13**, 764-45-4; **14**, 87373-90-8; **15**, 49651-56-1; **16**, 57295-88-2; **17**, 42848-09-9; **18**, 87373-91-9; **19**, 87373-92-0; **20**, 156-59-2; **21**, 40588-74-7; **22**, 764-44-3; **23**, 87373-93-1; **24**, 53715-35-8; **26**, 66566-71-0; **27**, 40920-18-1; **28**, 39137-72-9; **29**, 13046-50-9; **31**, 20890-80-6; **31** sulfone, 18723-83-6; **32**, 20890-79-3; **34**, 87373-94-2; **34** disulfone, 87373-97-5; **35**, 87373-95-3; **35** disulfone, 33998-47-9; **37**, 87373-96-4; **39**, 77159-30-9; Me_2CHSNa, 20607-43-6; MeSNa, 5188-07-8; trichloroethylene, 79-01-6; tetrachloroethylene, 127-18-4.

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[35] A. Immirzi and B. Perini, *Acta Crystallogr., Sect. A*, **A33**, 216 (1977).

[36] P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J. P. Declercq. "MULTAN 76. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", York, England and Louvain-la-Neuve, Belgium, 1976.

Structure Resonance Theory and Electrophilic Reactivity of Helicenes. Theoretical Correlations

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The partial rate factors of protodetritiation of four helicenes containing 26 different reaction sites are correlated with various reactivity indices, i.e., the Herndon structure count ratios, Dewar's reactivity numbers, and π cation localization energies. The results show that that Herndon structure count ratio is superior to the other two parameters in this application. Also, the data indicate that differences in positional reactivities in helicenes are influenced by both steric requirements and resonance energy differences between the π hydrocarbon and the respective intermediate. In addition, the observed correlations suggest that the regular increase in reactivity with ring size at a given site, except for the C(1) position, seems to be due to the effect of differences in resonance energies and not to the increased distortion of the aromatic rings as previously suggested.

Studies of protodetritiation of trihelicene (phenanthrene),[1] tetrahelicene,[2] pentahelicene,[3] and hexahelicene[4] in trifluoroacetic acid provided rate data for many positions of these compounds covering a reactivity range of about seven orders of magnitude (Chart I). These data are ideal to test the applicability of the simple parameterized molecular orbital and valence bond theories. In earlier applications the reactivities of many benzenoid hydrocarbons were successfully correlated with the algorithm ln SC(ratio), where SC(ratio) is the ratio of the principal resonance structures of a reaction intermediate (SC_I) to that of the reactant (SC_R). For example, the

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[1] Bancroft, K. C. C.; Bott, R. W.; Eaborn, C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 95.

[2] Le Guen, M. M. J.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1274.

[3] Le Guen, M. M. J.; Shafig, Y. E.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 803.

[4] Archer, W. J.; Shafig, Y. E.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 675.

0022-3263/83/1948-4800$01.50/0

Chart I

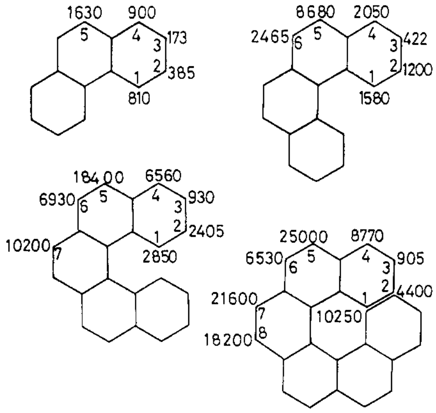


Table I. Partial Rate Factors of Protodetritiation of Helicenes and Various Resonance Energy Parameters[a]

compd (position)[b]	ln *f*	$-\sigma^+$	ln SC (ratio)	N_r	L^+_r
phenanthrene (1)[c]	6.697	0.331	0.875	1.961	2.366
phenanthrene (2)	5.953	0.294	0.875	2.041	2.454
phenanthrene (3)	5.153	0.254	0.788	2.181	2.498
phenanthrene (4)	6.802	0.336	0.956	1.860	2.318
phenanthrene (5)	7.396	0.365	0.956	1.796	2.299
tetrahelicene (1)	7.365	0.363	1.012	1.860	2.332
tetrahelicene (2)	7.090	0.350	0.916	2.065	2.461
tetrahelicene (3)	6.045	0.298	0.916	2.101	2.477
tetrahelicene (4)	7.626	0.376	1.012	1.835	2.312
tetrahelicene (5)	9.069	0.448	1.099	1.790	2.297
tetrahelicene (6)	7.810	0.385	1.012	1.859	2.320
pentahelicene (1)	7.955	0.393	1.019	1.869	2.397
pentahelicene (2)	7.785	0.384	0.990	2.036	2.454
pentahelicene (3)	6.835	0.337	0.932	2.130	2.483
pentahelicene (4)	8.789	0.434	1.073	1.829	2.311
pentahelicene (5)	9.820	0.485	1.196	1.741	2.283
pentahelicene (6)	8.844	0.436	1.046	1.834	2.314
pentahelicene (7)	9.230	0.456	1.149	1.852	2.320
hexahelicene (1)	9.235	0.456	1.066	1.876	2.338
hexahelicene (2)	8.389	0.414	0.999	2.047	2.456
hexahelicene (3)	6.808	0.336	0.981	2.111	2.479
hexahelicene (4)	9.079	0.448	1.083	1.831	2.311
hexahelicene (5)	10.127	0.500	1.218	1.758	2.287
hexahelicene (6)	8.784	0.434	1.083	1.838	2.315
hexahelicene (7)	9.980	0.493	1.190	1.807	2.306
hexahelicene (8)	9.809	0.484	1.232	1.873	2.314

[a] For the explanation of symbols, see the text. [b] See Chart I for numbering. [c] The positions 1, 2, 3, 4, and 5 indicated correspond to positions 4, 3, 2, 1, and 9, respectively, according to the IUPAC system rules for phenanthrene. This latter numbering is not used here as it is inconsistent with the higher homologues.

correlation coefficient for the relationship between the electrophilic reactivity index[6] σ^+ and ln SC(ratio) was reported[5] to be 0.977. This satisfactory correlation led to the conclusion that the difference in π resonance energies between the cationic intermediate and the reactant was the main factor controlling the difference in reactivity.[5] As the benzenoid hydrocarbons included in the correlations were free of ring distortions such as those present, for example, in hexahelicene,[7] it seemed of interest to extend the structure resonance theory calculations to the reported rate data of protodetritiation of helicenes.[1-4] Our objective is to cast some light on the relative importance of steric and resonance effects on the positional reactivities of benzenoid compounds in those cases where geometric steric factors might be expected to operate. Correlations of the same rate data with other HMO reactivity indices, i.e., the Dewar reactivity numbers (N_r)[8] and cation localization energies (L^+_r),[6] are also presented for comparison.

Results and Discussion

The logarithms of the partial rate factors of protodetritiation in trifluoroacetic acid at 70 °C, ln *f*, of tritium-labeled isomers of tri-, tetra-, penta-, and hexahelicenes are listed in Table I. These values were reported by Taylor et al.,[1-4] and they were considered to be accurate within ±5%. Along with these data, the logarithms of the structure count ratios, ln SC(ratio), for the reacting helicenes and the corresponding Wheland transition intermediates are given.[5] The structure counts of the neutral molecules, SC_R, were enumerated by the graph theoretical methods described previously.[9] The structure counts for the cationic intermediates, SC_I, were enumerated by determining the sum of the absolute values of the unnormalized coefficients of eigenvectors of the nonbonding molecular orbital for each cation.[9] In addition, the corresponding electrophilic position reactivity indices, σ^+, for the hydrocarbons examined and the HMO resonance energy indices, N_r and L^+_r, are also presented.

In this study, the values of σ^+ were calculated by eq 1,

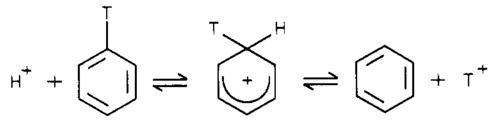
$$\sigma^+ = -(1/8.8)\log(k_{\mathrm{ArT}}/k_{\mathrm{C_6H_5T}}) \qquad (1)$$

where k_{ArT} and $k_{\mathrm{C_6H_5T}}$ are the rate constants for protodetritiation of the tritium-labeled helicene and benzene, respectively. The values of the cation localization energies L^+_r were taken from the literature,[1-4] and the values of the Dewar reactivity numbers N_r were calculated by eq 2,

$$N_r = 2(a_r + a_s)\beta \qquad (2)$$

where a_r and a_s are the normalized nonbonding molecular orbital (NBMO) coefficients of the transition intermediate at the points of attachment to the reaction site.[6,8]

In the HMO method, the cation localization energies L^+_r are known to correlate well with the ln *k* (or log *k*) values for various electrophilic aromatic substitutions.[10-13] In the structure resonance theory, a suitable reactivity index for the electrophilic exchange of the isotopes of hydrogen in aromatic hydrocarbons is the difference in the resonance energy ΔRE between the parent hydrocarbon and the corresponding intermediate.[14] It is assumed, of course, that the reaction involves the formation of a symmetrical Wheland transition intermediate. In such a case, the ln *f* or the equivalent σ^+ would be expected to correlate with the ΔRE values. In eq 3,



(3)

$$\Delta RE = RE_I - RE_R \qquad (4)$$

the parent hydrocarbon in the protodetritiation reaction is C_6H_5T and the corresponding intermediate is $C_6H_6T^+$.

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(5) Herndon, W. C. *J. Org. Chem.* **1975**, *40*, 3583.

(6) Streitwieser A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961; Chapter 11.

(7) De Rango, C.; Tsoucaris, G.; Declerq, J. P.; Germain, G.; Putzeys, J. P. *Cryst. Struct. Commun.* **1973**, *2*, 189.

(8) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3357.

(9) Herndon, W. C. *Tetrahedron* **1973**, *29*, 3.

(10) Párkányi, C.; Zahradník, R. *Tetrahedron Lett.* **1963**, 1897.

(11) Párkányi, C.; Dolejšek, Z.; Zahradník, R. *Collect Czech. Chem. Commun.* **1968**, *33*, 1211.

(12) Zahradník, R. *Chem. Listy* **1966**, *60*, 289.

(13) Zahradník, R.; Chalvet, O. *Collect Czech. Chem. Commun.* **1969**, *34*, 3402.

(14) Shawali, A. S.; Párkányi, C.; Herndon, W. C. *J. Org. Chem.* **1982**, *47*, 734.

Table II. Results of the Statistical Treatment of the ln f Data of Helicenes Using the ln SC (ratio) Parameter

series	n^a	$a_0{}^b$	$a_1{}^c$	r^d	$\pm s^e$
hexahelicenes	8	−1.893	9.869	0.882	0.509
pentahelicenes	7	−2.779	10.629	0.964	0.269
tetrahelicenes	6	−5.490	13.062	0.919	0.388
phenanthrenes	5	−3.685	11.331	0.916	0.348
all helicenes	26	−3.851	11.569	0.956	0.377

[a] The number of points. [b] Intercept. [c] Slope of the regression line. [d] Correlation coefficient. [e] Standard deviation.

The activation energy E_a for the reaction may be written[6] in the form:

$$E_a = C + \Delta\mathrm{RE} \tag{5}$$

where C is a constant characteristic of the electrophilic species and the displaced group. The activation energy, and therefore the rate, will be controlled by differences in ΔRE. The resonance energy of a given species has been shown to be given by eq 6,

$$\mathrm{RE} = a \ln \mathrm{SC} \tag{6}$$

where SC is the structure count of the species, and a is a proportionality constant.[15] Since

$$\ln k = C - E_a/RT \tag{7}$$

one can write

$$\ln k = a_0 + a_1 \ln \mathrm{SC_I} + a_2 \ln \mathrm{SC_R} \tag{8}$$

where $\mathrm{SC_I}$ and $\mathrm{SC_R}$ are the structure counts of the intermediate and the reactant, respectively. The constants in eq 8 can be determined by multiple regression analysis and sensible results require that the absolute values of a_1 and a_2 should not be too different. Under such conditions, eq 8 can be rewritten in the form

$$\ln k = a_0 + a \ln \mathrm{SC(ratio)} \tag{9}$$

where $\mathrm{SC(ratio)} = \mathrm{SC_I}/\mathrm{SC_R}$. Equation 9 is therefore expected to correlate the rate data for protodetritiation of helicenes provided that differences in resonance energies ΔRE are factors of prime importance in controlling differences in reactivities of the compounds under study.

When the ln f data were correlated by eq 8, the following linear relation was obtained:

$$\ln f = -3.722 - 10.635 \ln \mathrm{SC_R} + 10.888 \ln \mathrm{SC_I} \tag{10}$$

with a correlation coefficient $r = 0.945$ and a standard deviation $s = \pm 0.376$. The values of the constants a_1 and a_2 in this relation are indeed similar, their ratio being close to unity ($a_1/a_2 = 0.977$). This suggests that an acceptable correlation of the same rate data with the algorithm ln SC(ratio) would be expected. The least squares regression line corresponding to this correlation is expressed by eq 11,

$$\ln f = -3.851 + 11.569 \ln \mathrm{SC(ratio)} \tag{11}$$

$$r = 0.956;\ s = \pm 0.377$$

These correlations (eq 10, 11) indicate that the electrophilic reactivities of helicenes, similarly as of the other benzenoid hydrocarbons,[6] are influenced to a substantial degree by differences in resonance energies of the reactants and the cationic intermediate. This, however, does not necessarily mean that steric factors are insignificant. To look into this problem, the separate rate data for protodetritiation of each helicene were correlated by eq 9. The results of the statistical treatment of the data are summarized in Table II. As expected, a comparison of the values of the correlation coefficients and standard deviations of the relations obtained reveals that the rate data for hexahelicenes exhibit the poorest correlation with ln SC(ratio). Although this result seems to suggest that steric factors are probably more important in hexahelicene than in other helicenes, there is not clear-cut relationship between the correlation coefficients and the size of the molecules for other helicenes (with phenanthrene, r is only 0.916, whereas it is 0.964 in the case of pentahelicene).

Table III. Constants for Linear Correlations of the ln f Data for Various Positions in Helicenes Using Eq 9[a]

position	n	a_0	a_1	r	$\pm s$
1	4	−3.476	11.369	0.867	0.537
2	4	−8.709	16.945	0.967	0.266
3	4	−1.989	9.067	0.939	0.272
4	4	−10.290	17.812	0.996	0.088
5	4	−2.296	10.202	0.996	0.107

[a] For the explanation of symbols, see Table II.

Table IV. Statistical Treatment of the ln f Data Using Various Resonance Energy Parameters[a]

parameter	n	a_0	a_1	r	$\pm s$
ln SC (ratio)	26	−3.851	11.569	0.956	0.377
N_r	26	23.651	−8.168	−0.773	0.888
$L^+{}_r$	26	39.219	−13.189	−0.727	0.778

[a] For the explanation of symbols, see Table II.

To shed more light on this question, the correlations of ln f data for equivalent sites in the four helicenes with ln SC(ratio) were examined. The results of the statistical treatment of the data are given in Table III. As shown, satisfactory correlations are obtained for all sites except the 1-position. These results reveal that for positions having similar steric environments, the ln SC(ratio) would be a suitable reactivity index. Also, the satisfactory or acceptable correlations obtained show that a regular increase in reactivity of a given type of position with increasing ring size seems to be due to a regular decrease in differences in resonance energies with ring size. These findings contrast the conclusion made earlier[4] that the increase in positional reactivity within the helicene series with ring size is due primarily to the loss of ground state stability that results from an increasing distortion of the molecule. However, the fact that the constants a_0 and a_1 show a large variability for different types of positions may be related to particular steric contraints for each particular type of reaction site. A reexamination of the rate data for unstrained benzenoid hydrocarbons will be carried out in the near future with this point in mind.

Next, the correlations of the rate data for protodetritiation of helicenes with other resonance energy indices, i.e., the Dewar reactivity numbers and HMO cation localization energies, were considered. The results of the statistical treatment of the data for all 26 helicenes are summarized in Table IV. From the values of the correlation coefficients and standard deviations, it is obvious that the algorithm ln SC(ratio) correlates the data much better than N_r and $L^+{}_r$ for the C-2 position. According to the values given for such indices in Table I, it would be expected that small or no variations in rates of protodetritiation would be observed which is contrary to the experimental data. We conclude that predictions and detailed discussions of electrophilic reactivities for large aromatic hydrocarbons should not be based on the theoretical results of simplified molecular orbital methods.

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[15] Swinborne-Sheldrake, R.; Herndon, W. C.; Gutman, I. *Tetrahedron Lett.* **1975**, 755.

Even in unstrained systems, LCAO-MO-SCF calculations and valence bond-structure resonance theory give much better correlations of the rate data (r = 0.987 and 0.977, respectively) than do the Dewar reactivity numbers and HMO localization energies (r = −0.900 and −0.873) as reported previously.[5]

Acknowledgment. Cyril Pârkányi and William C. Herndon acknowledge the financial support of the Robert A. Welch Foundation.

Registry No. Hexahelicene, 187-83-7; pentahelicene, 188-52-3; tetrahelicene, 195-19-7; phenanthrene, 85-01-8; hydrogen, 1333-74-0.

Substitution at Tricoordinate Sulfur(IV). Rearrangement of Sulfinanilides to Anilino Sulfoxides[1]

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Seven N-methyl-N-aryl-p-toluenesulfinamides (**1**, 3-$Me_2NC_6H_4$; **2**, 3-$MeOC_6H_4$; **3**, 4-$MeOC_6H_4$; **4**, 3-MeC_6H_4; **5**, Ph; **6**, 3-ClC_6H_4; **7**, 3-FC_6H_4), N-(3-methoxyphenyl)-p-toluenesulfinamide (**8**), and two N-methyl-N-arylmethanesulfinamides (**9**, 3-$Me_2NC_6H_4$; **10**, 3-$MeOC_6H_4$) were prepared from the corresponding sulfinyl chloride and the substituted aniline. Sulfinanilides **2** and **7** were treated with alkyllithiums in vain attempts to induce rearrangement to the diaryl sulfoxides via endocyclic nucleophilic attack by carbon 2 of the aniline ring on sulfur. Instead, the alkyllithium cleaved the S–N bond to yield the aniline and alkyl p-tolyl sulfoxide. Upon treatment with gaseous HCl in chloroform, the sulfinanilides rearranged as follows: **1** gave 4-(dimethylamino)-2-(methylamino)-4′-methyldiphenyl sulfoxide (92% yield), **2** gave 2-methoxy-4-(methylamino)-4′-methyldiphenyl sulfoxide (26% yield) and 4-methoxy-2-(methylamino)-4′-methyldiphenyl sulfoxide (70% yield), **4** gave 2-methyl-4-(methylamino)-4′-methyldiphenyl sulfoxide (71% yield), **9** gave methyl 4-(dimethylamino)-2-(methylamino)phenyl sulfoxide (20% yield), and **10** gave methyl 2-methoxy-4-(methylamino)phenyl sulfoxide (5% yield). Sulfinanilides **3** and **5**–**8** did not rearrange. A tentative mechanism for the rearrangement is proposed.

Nucleophilic substitution at tricoordinate sulfur(IV), exemplified in this paper by sulfinyl sulfur, is a well-known much-studied reaction process of both synthetic importance and mechanistic interest (eq 1, n and m = 0, ±1,...).[2,3]

$$Nu{:}^{-n} + R-\overset{O}{\overset{\|}{S}}-L^{m} \longrightarrow R-\overset{O}{\overset{\|}{S}}-Nu^{1-n} + L{:}^{m-1} \qquad (1)$$

Inversion of configuration at the sulfur atom has been observed in most cases subjected to stereochemical analysis, but retention and racemization have also been noted. The inversion reaction may follow an S_N2-like pathway via a trigonal-bipyramidal intermediate with the nucleophilic (Nu), sulfur atom, and leaving group (L) approximately colinear, but other stereochemical situations are conceivable and have been proposed; e.g., both nucleophile and leaving group could be arranged equatorially. Retention reactions are thought to proceed via equatorial-apical disposition of Nu and L with perhaps limited pseudorotation (ligand permutation) of an intermediate. Racemization could proceed in a number of ways.

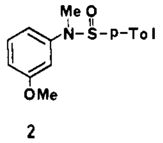
In order to investigate the stereochemistry of substitution as a function of the Nu–S–L angle, we synthesized the N-methyltoluene- and N-methylmethanesulfinanilides (**1**–**10**), which are listed in Table I.

We hoped that removal of a proton ortho to the amide nitrogen by a base would lead to endocyclic nucleophilic attack on sulfur by carbon to give a sulfoxide. For example, sulfinamide **2** would give sulfoxide **11** if endocyclic substitution occurred.

Table I. Sulfinanilides, $RS(O)NR_1C_6H_4X$

sulfinanilide	R	R_1	X	mp, °C	yield, %
1	p-tolyl	Me	3-Me_2N	*a*	
2	p-tolyl	Me	3-MeO	46.5–47.5[b]	96
3	p-tolyl	Me	4-MeO	83.5–84.5[b]	73
4	p-tolyl	Me	3-Me	68.5–69.5[b]	70
5	p-tolyl	Me	H	79.5–81.0[c]	58
6	p-tolyl	Me	3-Cl	63.5–65.0[b]	71
7	p-tolyl	Me	3-F	77.5–78.5[b]	63
8	p-tolyl	H	3-MeO	87–88[b]	84
9	Me	Me	3-Me_2N	*a*	
10	Me	Me	3-MeO	*d*	100

[a] Not isolated. [b] Satisfactory analyses (±0.3% of theory for C, H, and N) were obtained. [c] Lit.[7] mp 76–78 °C. [d] Unstable oil.



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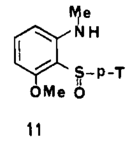

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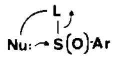
In endocyclic substitution the nucleophile and leaving group are bonded to one another so that the atom being substituted at, in our case, sulfur is transferred intramolecularly from L to Nu (**12**) in contrast to exocyclic reactions (**13**) where ring formation occurs and L is lost.[4–6]



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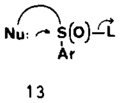

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[2] Mikolajczyk, M.; Drabowicz, J. *Top. Stereochem.* **1982**, *13*, 333–468.

[3] Kice J. L. *Adv. Phys. Org. Chem.* **1981**, *17*, 65–181.

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