the solid in carbon tetrachloride and determining the heat of mixing of the solution with an equimolecular quantity of chloroform (with respect to sulfoxide). Determinations were made also for comparable solutions of diethyl sulfoxide in carbon tetrachloride. The similarity of results for these heats of mixing[27] suggests that pentamethylene sulfoxide is at least comparable in basicity to tetramethylene sulfoxide, and may perhaps be slightly more basic. Thus the order of base strength indicated is 6- $\geq$ 5- $>$ 4-membered ring.

The 4-membered ring cyclic ketone or cyclic sulfoxide is decidedly weaker in basicity than any of the other ring members investigated in their respective series. This order is in marked contrast to that obtained for the cyclic ethers,[2a,3,4] *e.g.*, trimethylene oxide being a better base than tetrahydrofuran or tetrahydropyran. But the order, especially for the cyclic ketones, is in agreement with that observed for the lactones,[5] in which study it was shown that the carbonyl oxygen and not the alkoxyl oxygen entered into the formation of hydrogen bonds.[28] Thus it appears that the variation of electron distribution about the oxygen atom depends upon whether the oxygen is a member of the ring or is outside the ring.

In their studies, Barnard, Fabian and Koch[13] reported the S → O frequencies for several aliphatic and aromatic sulfoxides. All frequencies fell within the range 1047–1061 cm.$^{-1}$, and the authors remarked on the relative constancy of the bond in spite of widely differing substituents on the sulfur atom.[29] For the study reported in this paper, the frequencies for dimethyl- and diethyl sulfoxide are about in this same region (see Fig. 2), but the cyclic sulfoxides are well outside this range. The S → O frequency at 1092 cm.$^{-1}$ in trimethylene sulfoxide is higher than that of any other compound studied. In this respect it is like cyclobutanone which has a C=O frequency at 1775 cm.$^{-1}$, the highest of the ring series. The spectra of tetramethylene sulfoxide and especially of pentamethylene sulfoxide are more complex, several bands for the latter compound are in the region where the S → O frequency is expected. By determining the effect on the spectrum when first carbon tetrachloride and then chloroform were used as solvents, it was possible to choose that band due to S → O vibration (see Fig. 3). Thus the trend in the smaller ring compounds of decreasing C=O frequency with increasing ring size apparently is not carried over into the cyclic sulfoxides.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund Administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[27] The ampoule which could be accommodated inside the calorimeter was of limited size and generally contained no more than 10 cc. of sample. In the determinations involving solutions containing 17.55 and 35.93 moles % of pentamethylene sulfoxide in carbon tetrachloride, the total moles of the sulfoxide were 0.01474 and 0.02415, respectively. Determinations using these smaller quantities are subject to larger experimental error, and a difference of 20 cal./mole between results for diethyl sulfoxide and pentamethylene sulfoxide cannot be considered significant.

[28] R. L. Adelman and I. M. Klein, *J. Polymer Sci.*, **31**, 77 (1958), present data which indicate that perhaps alkoxyl oxygen rather than carbonyl oxygen is involved in solvent action on polyvinyl chloride. This point is discussed and references to other work on esters and lactones are given. Pratt and Matsuda, ref. 22, support the contention than the carbonyl oxygen in esters contributes more to the basicity.

[29] (a) C. C. Price and R. G. Gillis, THIS JOURNAL, **75**, 4750 (1953), show that the S–O bond frequency in methyl vinyl sulfoxide is at a shorter wave length than it is in methyl propyl sulfoxide; (b) C. W. N. Cumper and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956), report that the change in dipole moment (in the direction of the S–O bond) when the sulfide is converted to the sulfoxide is greater in aromatic than in aliphatic compounds. The analysis involves certain assumptions in the calculation of bond moments, and the authors point out that this conclusion is based on limited results.

ANN ARBOR, MICHIGAN AND
MANHATTAN, KANSAS

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY, UNIVERSITY OF NORTH CAROLINA]

Sulfur–Oxygen Scission *versus* Carbon–Oxygen Scission in Reactions of 2,4-Dinitrophenyl *p*-Toluenesulfonate and Related Esters with Nucleophilic Reagents[1]

BY J. F. BUNNETT[2] AND J. Y. BASSETT, JR.[3]

RECEIVED AUGUST 25, 1958

A number of mono- and dinitrophenyl esters of *p*-toluenesulfonic and mesitylenesulfonic acids have been found to undergo both sulfur–oxygen and carbon–oxygen scission in reactions with nucleophilic reagents. With 2,4-dinitrophenyl *p*-toluenesulfonate, the fraction of C–O scission varies according to the reagent used from 100% with sodium thiophenoxide to but 12% with sodium methoxide. The relative rates of C–O and S–O scission are not related to over-all nucleophilic reactivity as represented by *n* of the Swain and Scott treatment, but rather to reagent polarizability. London forces appear to facilitate attack on the dinitrophenyl carbon by reagents of higher polarizability. Methyl groups introduced *ortho* to the sulfonate sulfur atom have relatively little effect on the proportion of C–O to S–O scission. They appear to provide little or no steric hindrance to nucleophilic attack on sulfonate sulfur.

Esters of sulfonic acids are in general easily cleaved by nucleophilic reagents. It has long been known that either the sulfur–oxygen bond or the carbon–oxygen bond can be cleaved depending on the structure of the ester. Thus *alkyl* esters of sulfonic acids undergo C–O bond scission with formation of alkyl derivatives of the nucleophilic reagents while *aryl* esters customarily are attacked at sulfur,

[1] Research supported in part by the Office of Ordnance Research, U. S. Army. This work was presented in part at the American Chemical Society meeting in Miami, Florida, April, 1957.

[2] Department of Chemistry, Brown University, Providence, Rhode Island.

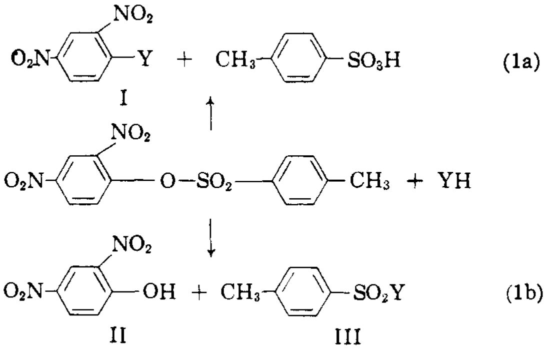
[3] R. J. Reynolds Fellow, 1956–1957. This manuscript is based on the Ph.D. thesis of J. Y. Bassett, Jr., October, 1957.

with S–O bond scission and formation of sulfonyl derivatives of the reagents.[4] 2,4-Dinitrophenyl *p*-toluenesulfonate, however, is an example of an aryl ester which is attacked at carbon (the 1-position of the phenolic moiety) owing to the strong activation of this position by the two nitro groups. This ester reacts with pyridine and with aniline to form C–O cleavage products in high yields.[5a] Reactivity in systems of this type has been discussed by Clark and Todd.[5b]

Of special interest to us was the report[6] that the reaction of 2,4-dinitrophenyl *p*-toluenesulfonate with sodium phenoxide yielded no dinitrodiphenyl ether but only phenyl *p*-toluenesulfonate. Thus S–O scission occurred in contrast to C–O scission by the reagents aniline and pyridine, as mentioned above. Furthermore, reactions of this dinitrophenyl ester with ammonia,[5a] with aniline hydrochloride[7] and with piperidine[8,9] have furnished mixtures of C–O and S–O scission products. These observations suggested that the occurrence of C–O *vs.* S–O scission depended on the reagent used. Our objective in this research was to gain further information about such dependence and about other factors affecting the mode of scission.

Reactions of 2,4-Dinitrophenyl *p*-Toluenesulfonate with Diverse Reagents.—Reactions of this ester with nucleophilic reagents YH may be represented as in Chart I.[10] It is clear that different products are obtained from C–O scission (equation 1a) than from S–O scission (equation 1b), and that the fraction of scission by each route can be established by determining yields of various products. This we have done for reactions of 2,4-dinitrophenyl *p*-toluenesulfonate with seven reagents. Results are summarized in Table I.

CHART I



In this work no effort was made to isolate *p*-toluenesulfonic acid (equation 1a). In all cases it was possible to isolate the 2,4-dinitrophenyl derivative I of the nucleophilic reagent, and the yield of I was taken to represent the amount of C–O scission. 2,4-Dinitrophenol (II) and the *p*-toluenesulfonyl derivative III were usually both isolable in comparable yields which represent the amount of S–O scission. With all reagents but one, the combined yields of S–O and C–O cleavage products were in excess of 90%. All yields represent actual weighed quantities of products having satisfactory melting points.

TABLE I

REACTIONS OF 2,4-DINITROPHENYL *p*-TOLUENESULFONATE WITH NUCLEOPHILIC REAGENTS[a]

		Actual yields (%) of products of		
		S–O scission[b]		C–O scission[b]
Reagent	Conditions	II	III	I
$C_6H_5S^-$	60% dioxane, 27°, 2 hr.	0	0	92
$CH_3COCHCO_2C_2H_5^-$	Tetrahydrofuran, 27°, 10 min.	0	0	93
$C_6H_5NH_2$	60% dioxane, 27°, 3.5 hr.	8	10	88
Piperidine[c]	67% acetone: 33% methanol, 0°, 2 hr.	23	25	72
Glycine ethyl ester	95% ethanol, 35°, 24 hr.	64[d]	24	30
$C_6H_5O^-$	60% dioxane, 27°, 2 hr.	67	67	32
CH_3O^-	67% acetone: 33% methanol, 0°, 5 min.	87	[e]	12

[a] See Experimental section for details. [b] See Chart I. [c] See also Table II. [d] This is partly a product of hydrolysis. [e] No attempt was made to isolate methyl *p*-toluenesulfonate.

TABLE II

THE SENSE OF CLEAVAGE OF 2,4-DINITROPHENYL *p*-TOLUENESULFONATE BY PIPERIDINE IN VARIOUS SOLVENTS[a]

Solvent	Yield of 2,4-dinitrophenylpiperidine, %
Methanol	55
67% CCl_4–33% methanol	55
60% dioxane–40% water	67
67% diethyl ether–33% methanol	71
67% $CHCl_3$–33% methanol	72
67% tetrahydrofuran–33% methanol	75
67% acetone–33% methanol	77
67% benzene–33% methanol	78
67% ethyl acetate–33% methanol	79
67% dioxane–33% methanol	80

[a] All runs analyzed after 5 hours reaction at 27°. Reaction can be assumed to be complete in every case.[9] The yields listed represent the percentage of C–O scission; subtraction from 100% gives the percentage of S–O scission.[11]

The results (Table I) show that the sense of cleavage of 2,4-dinitrophenyl *p*-toluenesulfonate is indeed dependent on the nucleophilic reagent. The extent of C–O scission varies from 100% (so far as we can tell from the experiment) with sodium thiophenoxide through a series of intermediate values to only 12% with sodium methoxide. There is a corresponding rise in the extent of S–O scission.

Solvent Effects in the Reaction with Piperidine.—It is easy to determine the sense of cleavage of 2,4-dinitrophenyl *p* - toluenesulfonate by piperidine through photometric measurements.[9] 2,4-Dinitro-

---

(4) C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951); E. E. Turner, L. G. Groves and G. I. Sharp, *ibid.*, 512 (1929); E. E. Turner and R. V. Henley, *ibid.*, 928 (1930).

(5) (a) F. Ullmann and G. Nadai, *Ber.*, **41**, 1870 (1908); (b) V. M. Clark and A. R. Todd, *J. Chem. Soc.*, 2023 (1950).

(6) E. T. Borrows, J. C. Clayton, B. A. Hems and A. G. Long, *ibid.*, S190 (1949).

(7) D. Klamann, *Ann.*, **583**, 63 (1953).

(8) F. Bell, *J. Chem. Soc.*, 609 (1931).

(9) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, THIS JOURNAL, **79**, 385 (1957).

(10) Active hydrogen atoms of YH, of 2,4-dinitrophenol and of *p*-toluenesulfonic acid are understood to be derived either from the reagent as introduced, from the solvent or from acids added after the main reaction.

(11) The figures listed in Table II are percentage of C–O scission, and it is assumed that the difference from 100% is the per cent. of S–O scission. For one solvent (67% acetone–33% methanol) the percentages so derived from photometric measurements were verified by product isolation (*cf.* Table I). It is most unlikely that any of the other solvents would have caused side reactions which would render the conclusions from photometric measurements incorrect.

phenylpiperidine, a product of C–O scission, is orange in solutions of moderate acidity whereas the starting ester and all the other cleavage products are colorless. The photometrically determined sense of cleavage in each of a number of solvent mixtures is displayed in Table II.[11] These data show that there is some variation in the ratio of C–O to S–O scission with change of solvent but not enough to change the position of piperidine in Table I. This result supports our feeling that the data of Table I reflect primarily differences in reagents and only to a minor extent differences in the solvents used.

The Effect of Changing Substituents in the Phenolic Moiety.—One would expect the rates of both C–O and S–O scission to be decreased by removal of one nitro group from the phenolic moiety of 2,4-dinitrophenyl *p*-toluenesulfonate, since both reactions are assisted by electron withdrawal from the reaction sites. Of the two reactions C–O scission would be expected to be the more sensitive to electronic effects; aromatic nucleophilic substitutions have especially high Hammett *rho*[12a] values (about +4 to +5).[12b,c,d] Thus removal of a nitro group from the phenolic moiety was predicted to cause a decrease in the fraction of C–O scission. As shown by comparison of the data of the top part of Table III with corresponding data in Table I, this prediction is borne out by the facts. Whereas the 2,4-dinitrophenyl ester undergoes total C–O scission by thiophenoxide ion, the *p*-nitrophenyl ester is cleaved in this manner only to the extent of about 25%. Piperidine (in 60% dioxane–40% water) causes 67% C–O cleavage of the 2,4-dinitrophenyl ester but only about 10% C–O cleavage of the *o*- or *p*-nitrophenyl ester.

TABLE III

REACTIONS OF ARYL ESTERS OF *p*-TOLUENESULFONIC AND MESITYLENESULFONIC ACIDS WITH NUCLEOPHILIC REAGENTS

Substituents in phenolic moiety	Reagent	Actual yields (%) of products of S–O scission ArOH	S–O scission Ar'-SO_2Y	C–O scission ArY
	Esters of *p*-toluenesulfonic acid			
4-Nitro	$C_6H_5S^-$ [a]	72	60[i]	25
	$CH_3COCHCO_2C_2H_5^-$ [b]	No reaction		
	Piperidine[c]	88	89	9
2-Nitro	Piperidine[c]	85	86	11
2,6-Dinitro-4-methyl	$C_6H_5S^-$ [d]	0	0	96
	Esters of mesitylenesulfonic acid			
4-Nitro	Piperidine[c]	53	55	39
2-Nitro	Piperidine[c]	57	60	36
2,4-Dinitro	Piperidine[e]	14	11	83
	Piperidine[f]	14	14	84
	Piperidine[g]			85
	CH_3O^- [h]	83		16

[a] 24 hr. in 60% dioxane–40% water at 100°. [b] 22 hr. in tetrahydrofuran at 65°. [c] 48 hr. in 60% dioxane–40% water at 46°. [d] 2 hr. in 60% dioxane–40% water at 27°. [e] 2.5 hr. in 60% dioxane–40% water at 0°. [f] 3 hr. in 67% acetone–33% methanol at 0°. [g] 3 hr. in methanol at 0°; photometric analysis. [h] 5 min. in 67% acetone–33% methanol at 0°. [i] See Experimental Section.

A somewhat different result was obtained with the acetoacetic ester anion. This reagent, which reacted readily with the 2,4-dinitrophenyl ester with total C–O scission, was unreactive with the *p*-nitrophenyl ester. The latter was recovered unchanged after 22 hours refluxing in tetrahydrofuran.

The 2,6-dinitro-4-methylphenyl ester resembled the 2,4-dinitrophenyl ester in giving only C–O cleavage with thiophenoxide ion.

Reactions of Aryl Mesitylenesulfonates.—Mesitylenesulfonic acid differs from *p*-toluenesulfonic acid in that its sulfo group is flanked on either side by *o*-methyl groups. These two methyl groups were expected to influence the sense of cleavage of aryl esters in two ways. Sterically, they were expected to hinder attack on sulfur and thus to decrease the fraction of S–O scission. Indeed, by analogy with the effect of *o*-methyl groups in benzoic esters,[13] total suppression of S–O scission was conceivable. Electronically, the electron-releasing methyl groups would surely decelerate nucleophilic displacement at both sites, but which displacement would be the more affected could not be predicted with certainty.

It was found (compare data in the lower part of Table III with data in the upper part and with data in Table I) that the two additional methyl groups do decrease the fraction of S–O scission, but not to a major extent. With the dinitrophenyl esters, the two *o*-methyl groups caused the fraction of S–O scission by piperidine to drop from 25 to 14% and by methoxide ion from 87 to 83%. With the *p*-nitrophenyl esters and again with the *o*-nitrophenyl esters, the two additional methyl groups reduced the percentage of S–O scission from about 87 to about 57%.

It is remarkable that the introduction of *o*-methyl groups has so little effect. The changes are of the modest order of magnitude that one might expect if only the electronic influences of the methyl groups were operating. That the effect of the methyl groups in reactions of the dinitrophenyl esters with methoxide ion is less than in reactions with piperidine does suggest that at least part of the over-all effect is steric in nature; methoxide ion is known to have less effective bulk than piperidine.[14,15] However, the discovery that *o-methyl groups have relatively little steric effect on nucleophilic attack on sufonate sulfur* is the impressive and important result of this part of our study.[16]

Discussion

The two most significant discoveries in this research are (a) that the steric effect of *o*-methyl groups on nucleophilic attack on sulfonate sulfur is very small, and (b) that the sense of cleavage of 2,4-dinitrophenyl *p*-toluenesulfonate depends very

---

[12] (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186; H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953); (b) E. Berliner and L. C. Monack, THIS JOURNAL, **74**, 1574 (1952); (c) J. F. Bunnett, H. Moe and D. Knutson, *ibid.*, **76**, 3936 (1954); (d) J. Miller, *Aust. J. Chem.*, **9**, 61 (1956).

[13] H. L. Goering, T. Rubin and M. S. Newman, THIS JOURNAL, **76**, 787 (1954).

[14] B. Capon and N. B. Chapman, *J. Chem. Soc.*, 600 (1957).

[15] J. D. Reinheimer and J. F. Bunnett, THIS JOURNAL, **81**, 315 (1959).

[16] This matter has been subjected to kinetic study; the results will be reported in another paper.

much on the nucleophilic reagent used. We shall now consider the implications of the latter effect.

First, it is of interest that no success attended efforts to interpret the results with reference to the equation of Swain and Scott[17] for correlation of rates of nucleophilic displacements. This equation has the form, $\log(k/k_0) = sn$, in which k and k_0 are rate coefficients for reaction of a substrate with any reagent and with water, respectively, s is a constant characteristic only of the substrate and n is a constant characteristic only of the reagent. In applying this equation to reactions of 2,4-dinitrophenyl *p*-toluenesulfonate with nucleophilic reagents, we must consider this ester as being two substrates, one susceptible to S–O scission and the other to C–O scission. One may then write

$$\log k_S = s_S n + \log k_{0,S}$$
$$\log k_C = s_C n + \log k_{0,C}$$

in which the subscripts S and C refer to reactions involving attack at those atoms. These equations can accommodate an inversion of relative rates of attack at the two centers if appropriately different k_0 and s values are chosen for the two equations. This is shown graphically in Fig. 1, in which the crossing of the two lines represents the point of inversion of relative rates of S–O and C–O scission. So far this looks pretty good; the difficulty with this treatment is that it requires the order of relative rates of S–O and C–O scission to be the same as the order of n-values of the reagents. If 2,4-dinitrochlorobenzene is chosen to evaluate n-values, and according to the Swain and Scott theory any substrate should be appropriate, the order of n-values is[18] $C_6H_5S^- > CH_3O^- >$ piperidine $> C_6H_5O^- > C_6H_5NH_2$. This bears no similarity whatsoever to the order of relative rates of C–O to S–O scission by these reagents, which is the order of arrangement in Table I.

Thus the Swain and Scott equation does not give an acceptable interpretation of the facts. This is not the first instance in which we have found their equation to be inadequate to account, even qualitatively, for experimental observations. An earlier instance concerned the observations that thiophenoxide ion is *much* more reactive than methoxide ion with 2,4-dinitrochlorobenzene but actually somewhat less reactive with *p*-fluoronitrobenzene.[15,19] These observations could fit the Swain and Scott treatment only if a high s-value were assigned to 2,4-dinitrochlorobenzene and an s-value of zero to *p*-fluoronitrobenzene. The latter assignment would imply that this substrate reacted at equal rates with all reagents, whereas in truth it shows considerable selectivity among reagents.[15,19]

The failure in two instances of the Swain and Scott equation[17] to represent the facts even qualitatively correctly shows that this equation has definite limitations. On the other hand, we note with pleasure that it provides a satisfactory empirical correlation of rates in a number of reaction series.

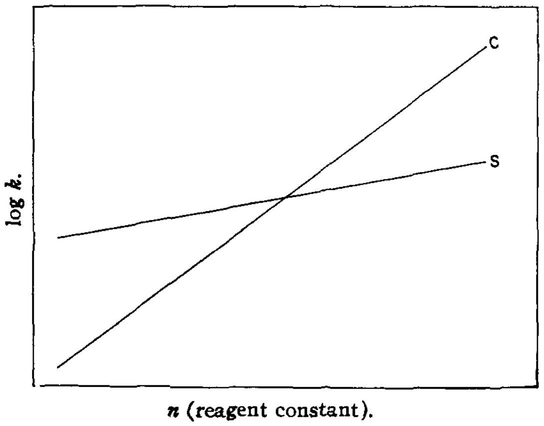


Fig. 1.—Attempt to interpret the inversion of relative rates of S–O and C–O scission in terms of the equation of Swain and Scott.[17] This treatment would require the ratios of S–O to C–O scission rates to be related to over-all reagent activity as represented by the reagent constant, n, but such is not the case.

Polarizability, rather than over-all nucleophilic reactivity as is represented by n in the Swain–Scott treatment, appears to be the reagent characteristic to which the ratio of C–O to S–O scission is related. The reagents which gave (see Table I) the most C–O scission are a sulfur anion and a carbanion; both types have high polarizability.[20] The reagents which gave the most S–O scission are oxygen anions whose polarizability is rather low. The reagents of intermediate character in respect to the ratio of C–O to S–O scission are also of intermediate polarizability. (It is the "effective" reagent polarizability, largely centered in the first atom of the reagent, of which we speak.)

Considerable evidence for the importance of polarizability as a component of nucleophilic character has been brought forth in recent years. Edwards[21] has shown that correlations of nucleophilic reactivity superior to those of Swain and Scott[17] can be obtained by use of the equation, $\log(k/k_0) = AP + BH$, in which P and H are reagent constants evaluated, respectively, from refraction data and acid dissociation constants. In effect, this equation says that nucleophilic reactivity is comprised of two main components: basicity represented by H and polarizability represented by P (the constants A and B represent substrate susceptibility to these two characteristics). Bunnett[22] has shown that reagents of high polarizability are especially reactive with substrates having atoms of high polarizability at or near the site of substitution and has interpreted this effect as being due to the operation of London forces in the transition state. Reinheimer and Bunnett[15] have obtained additional data supporting this interpretation from a study of the effects of *o*-substituents on nucleophilic aromatic substitutions.

With these ideas in mind, we interpret the results of Table I as follows: The region of the carbon

---

[17] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

[18] J. F. Bunnett and G. T. Davis, *ibid.*, **76**, 3011 (1954); **80**, 4337 (1958).

[19] C. W. Bevan and J. Hirst, *J. Chem. Soc.*, 254 (1956).

[20] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 119–137.

[21] J. O. Edwards, THIS JOURNAL, **76**, 1540 (1954); **78**, 1819 (1956).

[22] J. F. Bunnett, *ibid.*, **79**, 5969 (1957).

atom in the 1-position of the phenolic moiety of 2,4-dinitrophenyl *p*-toluenesulfonate is possessed of higher effective polarizability than the region of the sulfonate sulfur atom of this ester.[23] Reagents of high polarizability are therefore inclined, insofar as this aspect of nucleophilic reactivity is important, to attack this carbon atom with resultant C–O scission. Insofar as basicity of reagents is important, the sulfonate sulfur atom is more susceptible to attack (thus the predominance of S–O scission with methoxide ion), but the two substrate sites differ more in susceptibility to the polarizability than to the basicity characteristic of reagents.

In view of the proximity of the two substrate sites, it may seem improper to differentiate the region of the sulfur atom from the region of the carbon atom in the 1-position. Aside from its empirical justification, this differentiation derives support from the short range nature of London forces; the energy of attraction falls off with the sixth power of distance.[24] One or two additional bond lengths separation from the nitro group may, for instance, reduce London forces interaction of this group with reagents attacking sulfur to negligible magnitude.

Unfortunately, data now available are not sufficient for quantitative treatment of the results of Table I. Edwards' equation[21] would be used for such treatment.

Bordwell and co-workers[25] have shown that neopentyl *p*-toluenesulfonate suffers bimolecular C–O scission by some reagents, with formation of unrearranged neopentyl derivatives, and S–O scission by others. Reagents giving C–O scission included iodide ion, morpholine and several mercaptide ions; these are reagents of high polarizability. Methoxide ion caused S–O scission. There is a strong resemblance to our observations with 2,4-dinitrophenyl *p*-toluenesulfonate as recorded in Table I. We would also interpret their results in terms of the concepts underlying Edwards' equation and ultimately in terms of London forces interactions in the transition states for attack at neopentyl carbon. The vicinity of the neopentyl carbon is evidently a region of high polarizability, owing to the cluster of methyl groups nearby,[26] and there are favorable London forces interactions when reagents of high polarizability attack this carbon.

Reactions of Synthetic Interest.—For preparation of nitrophenyl esters of sulfonic acids, we have found it convenient to condense the sodium salt of the nitrophenol with the sulfonyl chloride in acetone solution or suspension.[9,27] The sodium salts of nitrophenols are easily obtained owing to their low solubility in aqueous sodium hydroxide. They are orange or red, and the progress of the condensation can be seen in the fading of the color. For the preparation of esters which are reactive with nucleophilic reagents, this method is superior to others in the literature.[5a,28]

The reactions of nitrophenyl *p*-toluenesulfonates with mercaptide reagents have utility for the preparation of aryl sulfides. We have shown (Tables I and III) that dinitrophenyl esters give nearly quantitative yields of sulfides and that even a mononitro ester, *p*-nitrophenyl *p*-toluenesulfonate, gives 25% of *p*-nitrodiphenyl sulfide. These reactions have special interest because they make nitroaryl sulfides accessible from nitrophenols which are sometimes more readily obtained than are nitrohalobenzenes. For example, 2-nitro-6-methylphenol is more accessible than 2-nitro-6-methylchlorobenzene.[29a] Bielig and Reidies[29b] have shown that dinitroaryl sulfides can also be obtained in good yield from dinitroarylpyridinium salts which in turn are sometimes obtained from dinitroaryl esters of sulfonic acids. In some cases our method of direct reaction with the ester is to be preferred.

Experimental

Materials.—Piperidine and tetrahydrofuran were purified by refluxing over sodium metal for 6 hours and then distilling from sodium. Reagent grade methanol was dried by the magnesium methoxide method. Dioxane was purified by treatment with potassium hydroxide and sodium chloride to remove water, refluxing over sodium metal for 4 days and final distillation from sodium metal. Ethyl acetoacetate and aniline were freshly distilled before being used. Practical grade *p*-toluenesulfonyl chloride was purified by the method of Pelletier.[30] Mesitylenesulfonyl chloride was prepared by the method of Demeny.[31]

Sodium Salts of Nitrophenols.—The nitrophenol was dissolved in a hot 10% solution of sodium hydroxide in water. The crystals formed on chilling were collected, washed with three small portions of ice-water and air-dried. Nitrophenol in the liquors was easily recovered by acidification and ether extraction. Some of the sodium salts so obtained are hydrates.[32]

Nitrophenyl Esters of Sulfonic Acids.—2,4-Dinitrophenyl *p*-toluenesulfonate was prepared as follows[9]: ten grams (0.053 mole) of *p*-toluenesulfonyl chloride was dissolved in 150 cc. of acetone in a three-neck flask equipped with a condenser and a stirrer. Sodium 2,4-dinitrophenoxide monohydrate[32] (11.9 g., 0.053 mole) was added and the slurry was stirred at reflux. As the reaction proceeded the solution turned from deep orange to pale yellow and the solid material changed from deep yellow to white. When there was no more yellow solid remaining (about an hour after the start of reaction), the mixture was poured into 500 cc. of ice and water. The light yellow solid which separated was collected and recrystallized from ethanol with use of decolorizing charcoal. The ester was obtained as pale yellow crystals, m.p. 123–124° (lit.[33] 124°), in the amount of 15.7 g. (88%).

The following esters were made by the same procedure: 4-nitrophenyl *p*-toluenesulfonate, m.p. 96–97° (lit.[34] 97°), yield 96%; 2-nitrophenyl *p*-toluenesulfonate, m.p. 81–83° (lit.[35] 81–82°), yield 83%; 2,4-dinitrophenyl mesitylene-

---

[23] The 2-nitro group is probably a major contributor to high polarizability in the region of the 1-position. There is evidence that an *o*-nitro group has high effective polarizability.[15]

(24) O. K. Rice, "Electronic Structure and Chemical Binding," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 354; J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. I, Longmans, Green and Co., London, 1949, p. 741.

(25) F. G. Bordwell, B. M. Pitt and M. Knell, This Journal, **73**, 5004 (1951); Absts. Am. Chem. Soc. Meeting, Philadelphia, Pa., April, 1950, p. 67L.

(26) See also W. M. Schubert and J. Robins, This Journal, **80**, 559 (1958).

(27) F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 452 (1951).

(28) W. Aorsche and E. Feske, *Ber.*, **60**, 157 (1927); J. H. Looker, *J. Org. Chem.*, **17**, 510 (1952).

(29) (a) Unpublished work by Mr. R. P. Blair; (b) H.-J. Bielig and A. Reidies, *Chem. Ber.*, **89**, 550 (1956).

(30) S. W. Pelletier, *Chemistry & Industry*, 1034 (1953).

(31) L. Demeny, *Rec. trav. chim.*, **50**, 51 (1931).

(32) (a) J. Fritzsche, *J. prakt. Chem.*, **73**, 305 (1906); **75**, 268 (1907); (b) H. Hubner and W. Schneider, *Ann.*, **167**, 98 (1873).

(33) K. Freudenberg and H. Hess, *ibid.*, **448**, 129 (1926).

(34) E. Bamberger and A. Rising, *Ber.*, **34**, 241 (1901).

(35) F. Ullmann and O. Lowenthal, *Ann.*, **332**, 63 (1904).

sulfonate, m.p. 121–123°, yield 80% (*Anal.* Calcd. for $C_{15}H_{14}N_2O_7S$: C, 49.17; H, 3.85. Found[36]: C, 49.17; H, 3.89); 4-nitrophenyl mesitylenesulfonate, m.p. 149–150°, yield 91% (*Anal.* Calcd. for $C_{15}H_{15}NO_5S$: C, 56.07; H, 4.71. Found[36]: C, 55.90; H, 4.48); 2-nitrophenyl mesitylenesulfonate, m.p. 101–102°, yield 75% (*Anal.* Calcd. as above. Found[36]: C, 56.23; H, 4.76).

Reactions Summarized in Table I.—The general procedure involved reaction of 1.0 g. of the ester with a three to five mole excess of the nucleophilic reagent in 60 cc. of the solvent, as indicated. The amine reagents were added as such. Sodium methoxide was added as a solution in methanol. Sodium phenoxide and thiophenoxide were generated by adding phenol or thiophenol (in excess to prevent hydrolysis by free hydroxide ion) to sodium hydroxide in aqueous dioxane. Sodioacetoacetic ester was generated by reaction of acetoacetic ester with sodium hydride in tetrahydrofuran. Temperatures and times for the various reactions are shown in Table I. At the end of reaction, dilute mineral acid was added and the mixture was evaporated to dryness at reduced pressure. The residue was taken up in benzene and separated by extraction into neutral and acidic fractions which were separately crystallized or chromatographed on alumina, unless otherwise noted below. The separation of products from any reaction was not considered acceptable until at least 90% of the starting ester could be accounted for in the products from at least two identical reaction mixtures. Every product was identified by its melting point and by observation that the mixed melting point with an authentic sample was not depressed. Details about the various experiments are: With sodium thiophenoxide: only 2,4-dinitrodiphenyl sulfide, m.p. 120–121° (lit.[37] 120–121°) could be isolated.

With sodioacetoacetic ester: only ethyl α-(2,4-dinitrophenyl)-acetoacetate, m.p. 94–95° (lit.[38] 94°), could be isolated.

With aniline: *p*-toluenesulfonanilide, m.p. 102–104° (lit.[39] 103°), and 2,4-dinitrodiphenylamine, m.p. 156–157° (lit.[40] 156°), and 2,4-dinitrophenol, m.p. 110–113° (lit.[32b] 112–114°), were isolated.

With piperidine: *p*-toluenesulfonpiperidide, m.p. 97–98° (lit.[41] 98°), 2,4-dinitrophenol, m.p. 110–113°, and 2,4-dinitrophenylpiperidine (separated from the other products by taking advantage of its solubility in concentrated hydrochloric acid), m.p. 91–92° (lit.[42] 92°), were isolated.

With glycine ethyl ester: The solvent was 95% ethanol set to a *p*H of 6.3 with a sodium acetate–acetic acid buffer. The products isolated were 2,4-dinitrophenol, m.p. 111–113°, the ethyl ester of N-(2,4-dinitrophenyl)-glycine, m.p. 143–145° (lit.[43] 144°), and N-*p*-toluenesulfonylglycine, m.p. 145–148° (lit.[44] 147°). It was separately shown that the expected ethyl ester of the last product was hydrolyzed under the conditions of the isolation procedure. The fact that the yield of 2,4-dinitrophenol is much in excess of the yield of N-*p*-toluenesulfonylglycine is interpreted as indicating that about 40% of the 2,4-dinitrophenyl *p*-toluenesulfonate was hydrolyzed under the conditions of reaction.

With sodium phenoxide: 2,4-dinitrophenol, m.p. 111–114°, phenyl *p*-toluenesulfonate, m.p. 94–95° (lit.[45] 95°), and 2,4-dinitrodiphenyl ether, m.p. 70–71° (lit.[46] 70°), were isolated. The last product was isolated by crystallization procedures; it was found to be destroyed during chromatography on untreated chromatographic alumina.

With sodium methoxide: 2,4-dinitrophenol, m.p. 113–115°, and 2,4-dinitroanisole, m.p. 86–87° (lit.[47] 87°), were isolated. No effort was made to isolate methyl *p*-toluenesulfonate since this ester was expected to react rapidly with sodium methoxide.

Reactions Summarized in Table III.—The general procedure for reaction with any reagent was the same as described for reactions with 2,4-dinitrophenyl *p*-toluenesulfonate. Nitrophenylpiperidines were isolated by taking advantage of their solubility in concentrated hydrochloric acid. Details about the various experiments are: 4-nitrophenyl *p*-toluenesulfonate with sodium thiophenoxide: The products isolated were *p*-nitrophenol, m.p. 112–114° (lit.[48] 113–114°), *p*-nitrodiphenyl sulfide, m.p. 55–56° (lit.[49] 54°), and diphenyl disulfide, m.p. 60–62° (lit.[50] 60°). The last is presumably a secondary product from action of thiophenoxide ion on the primary product, phenyl *p*-toluenethiosulfonate.[51] The yield of disulfide was 60%, calculated on the assumption of this mode of genesis.

4-Nitrophenyl *p*-toluenesulfonate with piperidine: The products isolated were *p*-nitrophenol, m.p. 111–113°, *p*-toluenesulfonylpiperidide, m.p. 97–100°, and *p*-nitrophenylpiperidine, m.p. 102–104° (lit.[42] 106°).

2-Nitrophenyl *p*-toluenesulfonate with piperidine: The products isolated were *o*-nitrophenol, m.p. 41–44° (lit.[52] 44–45°), *p*-toluenesulfonylpiperidide, m.p. 97–99°, and *o*-nitrophenylpiperidine, m.p. 77–80° (lit.[42] 79–80°).

2,6-Dinitro-4-methylphenyl *p*-toluenesulfonate with sodium thiophenoxide: The only product isolated was 2,6-dinitro-4-methyldiphenyl sulfide, m.p. 123–124°, a new compound. An authentic sample for mixed melting point determination was prepared from reaction of sodium thiophenoxide with 4-chloro-3,5-dinitrotoluene,[12b] with recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_{10}N_2O_4S$: C, 53.78; H, 3.47. Found[36]: C, 53.85; H, 3.42.

4-Nitrophenyl mesitylenesulfonate with piperidine: The products isolated were *p*-nitrophenol, m.p. 111–113°, *p*-nitrophenylpiperidine, m.p. 103–105°, and mesitylenesulfonpiperidide, m.p. 47–49°. The last is a new compound; an authentic sample of m.p. 49–51° was prepared by reaction of mesitylenesulfonyl chloride with piperidine.

Anal. Calcd. for $C_{14}H_{21}NO_2S$: C, 62.88; H, 7.92. Found[36]: C, 62.46; H, 7.80.

2-Nitrophenyl mesitylenesulfonate with piperidine: The products isolated were *o*-nitrophenol, m.p. 41–44°, mesitylenesulfonpiperidide, m.p. 47–49°, and *o*-nitrophenylpiperidine, m.p. 76–79°.

2,4-Dinitrophenyl mesitylenesulfonate with piperidine: The products isolated were 2,4-dinitrophenol, m.p. 111–114°, mesitylenesulfonpiperidide, m.p. 49–51°, and 2,4-dinitrophenylpiperidine, m.p. 90–92°.

2,4-Dinitrophenyl mesitylenesulfonate with sodium methoxide: The products isolated were 2,4-dinitrophenol, m.p. 112–114°, and 2,4-dinitroanisole, m.p. 83–86°. No effort was made to isolate methyl mesitylenesulfonate because of the likelihood that this methyl ester reacted further with sodium methoxide.

CHAPEL HILL, N. C.

---

[36] All analyses by Micro-Tech Laboratories, Skokie, Ill.

[37] R. W. Bost, J. O. Turner and R. D. Norton, THIS JOURNAL, **54**, 1985 (1932).

[38] B. B. Dey and Y. G. Doraiswami, *J. Indian Chem. Soc.*, **10**, 309 (1933).

[39] R. Otto, *J. prakt. Chem.*, **47**, 369 (1893).

[40] E. J. Hoffman and P. A. Dame, THIS JOURNAL, **41**, 1016 (1919).

[41] H. Staudinger and H. Schneider, *Ber.*, **56**, 699 (1923).

[42] E. Lellman and W. Geller, *ibid.*, **21**, 2283 (1888).

[43] E. Abderhalden and P. Blumberg, *Z. physiol. Chem.*, **65**, 320 (1910).

[44] E. Fischer, *Ann.*, **398**, 117 (1913).

[45] R. Otto, *Ber.*, **19**, 1833 (1886).

[46] L. C. Raiford and J. C. Colbert, THIS JOURNAL, **48**, 2660 (1926).

[47] C. Willgerodt, *Ber.*, **12**, 763 (1879).

[48] P. Wagner, *ibid.*, **7**, 77 (1874).

[49] C. Willgerodt and M. Klinger, *J. prakt. Chem.*, **85**, 194 (1912).

[50] C. Vogt, *Ann.*, **119**, 150 (1861).

[51] R. Connor, in H. Gilman, "Organic Chemistry," 2nd ed., Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 908.

[52] G. A. Hulett, *Z. physik. Chem.*, **28**, 666 (1899).