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

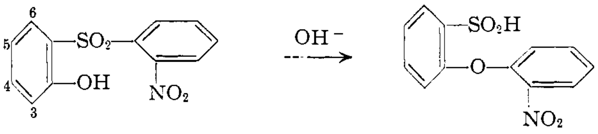
# Steric Acceleration through Regulation of Rotational Conformation: The Smiles Rearrangement[1,2]

BY J. F. BUNNETT AND TOSHIHIKO OKAMOTO[3]

RECEIVED MAY 14, 1956

The rate of rearrangement of a 2-hydroxy-2'-nitrodiphenyl sulfone to a 2-(*o*-nitrophenoxy)-benzenesulfinic acid is increased about 500,000-fold by the introduction of a methyl chloro or bromo substituent in the 6-position. Since both electron-releasing and electron-attracting 6-substituents cause similar tremendous increases in rate, the origin of the acceleration is steric and not electronic. The mechanism of the acceleration is discussed.

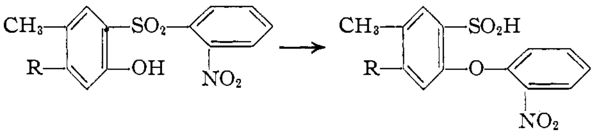
In 1937, McClement and Smiles[4] reported that the Smiles rearrangement of 2-hydroxy-2'-nitrodiphenyl sulfones to 2-(*o*-nitrophenoxy)-benzenesulfinic acids is accelerated by methyl groups in the 6-position. The cause of the acceleration, they said, was electron-release from the methyl group to the sulfone bridge which thereby was rendered less able to draw electrons from the ionized 2-hydroxy group. In consequence, they explained, the nucleophilic reactivity of the ionized hydroxy group was greater than it would otherwise have been, and the reaction went faster.[5]



Bunnett and Zahler[6] considered this explanation unconvincing, and showed that the acceleration could be interpreted more agreeably as a steric effect, that is, as a consequence of the *bulk* of the 6-methyl groups. The element of proof was lacking from their argument, however, and one of the aims of this work was to establish whether or not the acceleration actually arises from the size rather than from the electron-releasing character of 6-methyl groups. Another purpose was to describe the acceleration more exactly than McClement and Smiles had done.[7]

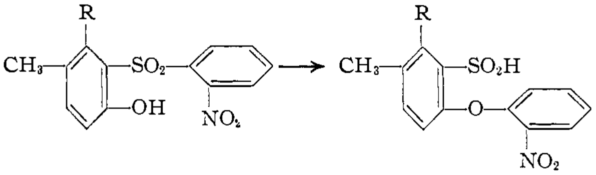
It was reasoned that if the acceleration is really due to the bulk rather than the electron-releasing effect of 6-methyl groups, then groups of comparable size but opposite electronic effect should also have an accelerating influence. On the other hand, if the acceleration were due to an unusual sensitivity of the reaction to the electronic influence of 6-substituents, the introduction of an electron-attracting group in that position should strongly decelerate the reaction. Thus, if the introduction of a 6-bromo or 6-chloro substituent caused a big increase in rearrangement rate, the effect would be shown to be steric, while a big decrease in rate would indicate that the effect was electronic.

The former proved to be the case, gratifying our expectations, and it then became desirable to have a means of estimating the normal electronic effect of 6-substituents on the reaction rate. For this purpose the kinetic effect of the same substituents in the 4-position was determined. The 4- and 6-positions are both *meta* to the phenolic hydroxy group while one is *ortho* and the other *para* to the sulfone bridge. As a first approximation, the electronic effect of a 6-substituent may be taken as equal to that of the same substituent in the 4-position.



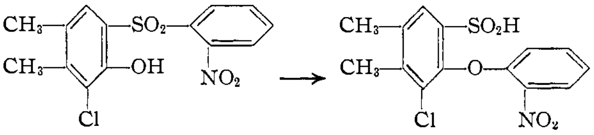
IVa, R = H
IVb, R = CH₃
IVc, R = Cl
IVd, R = Br

VIa, R = H
VIb, R = CH₃
VIc, R = Cl
VId, R = Br

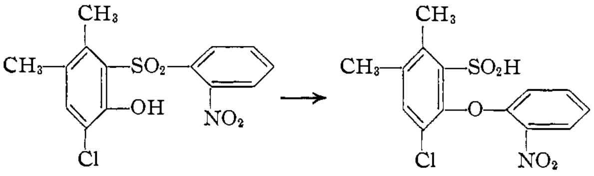


Vb, R = CH₃
Vc, R = Cl
Vd, R = Br

VIIb, R = CH₃
VIIc, R = Cl
VIId, R = Br



XIX XX



XVb XVIb

The sulfones chosen for kinetics study comprised four pairs of isomers (IVb and Vb, IVc and Vc, IVd and Vd, and XIX and XVb) which have a methyl, chlorine or bromine substituent first in the 4- and then in the 6-position. All of them possess a 5-methyl group for reasons of convenience in synthesis. The parent sulfone (IVa) having both the 4-

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[1] Described in part in a preliminary communication: T. Okamoto and J. F. Bunnett, *J. Org. Chem.*, **21**, 487 (1956).

[2] Presented in part to the Southeastern Regional Meeting, American Chemical Society, Columbia, S. C., November, 1955.

[3] On leave from the Pharmaceutical Institute, University of Tokyo, 1954–1956; grateful recipient of a Fulbright travel grant.

[4] C. S. McClement and S. Smiles, *J. Chem. Soc.*, 1016 (1937).

[5] In a series of researches on this and related rearrangements, summarized by Bunnett and Zahler,[6] Smiles and his co-workers demonstrated adequately that the function of the promoting base is to convert the hydroxy group to the corresponding ion which then effects an intramolecular nucleophilic displacement at the 1'-carbon to form the anion of the sulfinic acid product.

[6] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 369 (1951).

[7] McClement and Smiles estimated rates rather roughly, and their measurements indicate only that sulfones with 6-methyl groups rearrange, in general, more than ten times as fast as sulfones with a vacant 6-position.

and the 6-position unsubstituted was also prepared for study. The preparation of these sulfones and an examination of their rearrangement reactions are described in an accompanying paper.[8] The several compounds are given the same roman numeral designations in both papers.

## Experimental

**Rate Measurements by the Titration Technique.**—A solution of about 0.001 mole of sulfone IVa or IVb in 50% aqueous dioxane (by weight) was combined with enough of a standard solution of sodium hydroxide in 50% dioxane to provide 1.2 moles of base per mole of sulfone, and the solution was made up to a volume of 250 cc., shaken thoroughly, and returned to the thermostat. All components of the reaction mixture were brought to thermostat temperature before being combined. Aliquots (25 cc.) were removed at recorded times, and discharged into beakers containing excess dilute sulfuric acid in standard amount. The quenched solutions were back-titrated potentiometrically with standard aqueous sodium hydroxide solution. The plot of *p*H *vs.* volume of titrant showed two breaks: one with the steepest slope at about *p*H 7, corresponding to neutralization of excess sulfuric acid plus the sulfinic acid which had been formed, and a second with steepest slope at about *p*H 11, corresponding to neutralization of the phenolic hydroxyl of unreacted IVa or IVb. The second break occurred at the same volume for all samples within a given run. "Infinity" samples showed a single break at the volume characteristic of the second break. The logarithm of the difference in volume of titrant for the two breaks was plotted against time. The resulting plots were straight lines, the slopes of which were multiplied by 2.303 to get the first-order rate coefficients.

In a set of runs with sulfone IVa at 46° (Table I), the effect of varying the sodium hydroxide concentration was studied. The rate is not dependent on sodium hydroxide concentration within the range studied. This means that 1.2 moles of sodium hydroxide per mole of phenolic sulfone is sufficient to transform the phenol completely into the corresponding phenoxide ion.

TABLE I

RATE COEFFICIENTS FOR SMILES REARRANGEMENTS

| Sulfone | Temp., °C. | Moles NaOH per mole sulfone | Analytical method[a] | No. runs | Mean rate coefficient, min.$^{-1}$[b] |
|---|---|---|---|---|---|
| IVa | 25.00 | 1.2 | Titration | 3 | $1.38 \pm 0.02 \times 10^{-3}$ |
| IVa | 46.00 | 1.2 | Titration | 3 | $1.93 \pm 0.08 \times 10^{-2}$ |
| | | 1.5 | Titration | 1 | $2.02 \times 10^{-2}$ |
| | | 2.0 | Titration | 1 | $1.97 \times 10^{-2}$ |
| | | 2.5 | Titration | 1 | $1.83 \times 10^{-2}$ |
| | | 1.2 | Polarography<br>*p*H 9.2 | 2 | $1.92 \pm 0.08 \times 10^{-2}$ |
| | | 1.2 | Polarography<br>*p*H 6.5; −0.60v. | 2 | $2.33 \pm 0.12 \times 10^{-2}$ |
| IVb | 25.00 | 1.2 | Titration | 3 | $1.26 \pm 0.04 \times 10^{-3}$ |
| IVb | 46.00 | 1.2 | Titration | 5 | $1.66 \pm .06 \times 10^{-2}$ |
| IVc | 46.00 | 1.2 | Polarography<br>*p*H 5.0; −.60v. | 2 | $1.44 \pm .01 \times 10^{-3}$ |
| IVc | 67.2 | 1.2 | Polarography<br>*p*H 5.0; −.60v. | 2 | $1.72 \pm .04 \times 10^{-2}$ |
| IVd | 46.00 | 1.2 | Polarography<br>*p*H 6.0; −.65v. | 2 | $1.23 \pm .01 \times 10^{-3}$ |
| Vb | 0.0 | 1.2 | Too fast to measure | | |
| Vc | .0 | 1.2 | Polarography<br>*p*H 5.0; −.50v. | 2 | $9.2 \pm 1.3 \times 10^{-1}$ |
| Vd | .0 | 1.2 | Polarography<br>*p*H 5.0; −.50v. | 2 | $2.1 \pm 0.6$ |
| XVb | .0 | 1.2 | Polarography<br>*p*H 4.0; −.60v. | 2 | $1.29 \pm 0.01 \times 10^{-1}$ |
| XVb | 14.4 | 1.2 | Polarography<br>*p*H 4.0; −.60v. | 2 | $8.3 \pm 1.0 \times 10^{-1}$ |
| XIX | 46.00 | 1.2 | Polarography<br>*p*H 6.0; −.70v. | 2 | $1.0 \pm 0.07 \times 10^{-3}$ |
| XIX | 67.2 | 1.2 | Polarography<br>*p*H 6.0; −.70v. | 3 | $1.45 \pm 0.04 \times 10^{-2}$ |

[a] Voltages are *vs.* S.C.E. [b] The average deviation is given.

It was not practical to determine rates of rearrangement of the halogen-containing sulfones by the titration technique. The first breaks in the titration curves were so shallow that the end-points could not be located with certainty. Only rough estimates of rates could be obtained; the rates reported in the preliminary communication[1] were estimated in this way. It may be noted, though, that the estimates obtained from titration were in all cases confirmed as to general magnitude by the more satisfactory polarographic determinations.

**Rate Measurements by the Polarographic Technique.**—It was expected that the half-wave potential for reduction of the nitro group would be different in a sulfinic acid and in the sulfone from which it was derived. This proved to be the case, but in many cases it was necessary to choose the *p*H for polarographic measurements with care in order to realize a satisfactory difference in reduction potentials. We therefore determined, for each pair of sulfone and sulfinic acid derived therefrom, the variation of reduction potential with *p*H. In the cases of compounds with a vacant 6-position, the half-wave potential of the sulfinic acid increased smoothly in a nearly linear fashion with *p*H while the reduction potential of the sulfone increased at first, remained nearly constant in the region of *p*H 4 to 7, and finally increased again. A typical plot is shown in Fig. 1. In the cases of compounds bearing 6-substituents, both the sulfone and the sulfinic acid derived therefrom showed a similar smooth increase in reduction potential with *p*H, and at no *p*H was there a great difference in reduction potentials. A typical case is shown in Fig. 2. However, in every case it was possible to choose a *p*H at which there was a sufficient difference in reduction potentials to be made the basis of an analytical method. Finally, from the polarographic curves for each pair of sulfone and sulfinic acid at the *p*H chosen, a potential was chosen at which there was a maximum difference in current. Sometimes, this was on the ascending portion of the curve for both the sulfone and the sulfinic acid. It was shown in several cases that there was a linear relationship between current and concentration for known mixtures of sulfone and sulfinic acid derived therefrom.

For these preliminary polarographic explorations, $1 \times 10^{-4}$ mole of the sulfone or sulfinic acid was dissolved in 50 cc. of 50% dioxane. The resulting solution was diluted with a solution of Prideaux buffer,[9] 0.2 mole/l. in 25% dioxane and adjusted to the desired *p*H by addition of sodium hydroxide, to a volume of 100 cc. Two or three drops of a 1% solution of Triton X-100 (Rohm and Haas Co.) were added per 10 cc. of the resulting solution before or as it was placed in the polarographic cell.

All polarographic measurements were made in a cell cooled by ice-water circulated through a surrounding jacket. Also, nitrogen gas was bubbled through every solution examined polarographically for about three minutes before measurements were made.

For actual kinetics runs, $1 \times 10^{-4}$ mole of a sulfone was combined with $1.2 \times 10^{-4}$ mole of sodium hydroxide (supplied as a standard solution in 50% dioxane) and the solution was diluted to 50 cc. with 50% dioxane. All components of the reaction mixture were brought to thermostat temperature before being mixed, and the flask containing the reaction solution was returned to the thermostat at once after being vigorously shaken to ensure good mixing. Samples were removed by pipet at recorded times and combined with an equal volume of Prideaux buffer[9] (0.2 mole/l. in 25% dioxane and adjusted to the *p*H desired for polarographic measurements by addition of sodium hydroxide). In cases of very fast reactions, the resulting quenched solutions were kept in an ice-bath until the run was completed and then polarographic measurements were made without delay. Quenched aliquots from the slower reactions were kept at about −20° in a freezing cabinet until all the desired samples had been obtained, and they were then all warmed to 0° before polarographic measurements were made. Two or three drops of a 1% solution of Triton X-100 were added per 10 cc. of quenched solution before a portion of it was placed in the polarographic cell. The potential was set at the selected value, and the current for each sample was recorded during a period of about five drops. The average between the maximum and minimum currents dur-

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(8) T. Okamoto and J. F. Bunnett, THIS JOURNAL, **78**, 5357 (1956).

(9) E. B. R. Prideaux, *Proc. Roy. Soc.* (*London*), **A92**, 463 (1916).

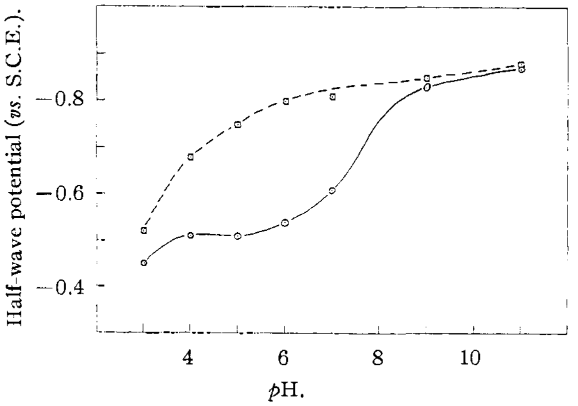

Fig. 1.—Typical variation of reduction potential with *p*H for a sulfone *lacking* a 6-substituent and the related sulfinic acid: solid line, sulfone XIX; broken line, sulfinic acid XX.

ing the life of a typical drop was taken as the current for that sample. The logarithm of $(I - I_\infty)$ was plotted *vs.* time, and the resulting plots approximated a straight line, although there was more scatter than in corresponding plots from the titration technique with IVa or IVb. The slope of the line was determined by the method of least squares and multiplied by 2.303 to obtain the rate coefficient.

Rate coefficients determined by both techniques are listed in Table I. For sulfone IVa, both techniques were used and the agreement between rate coefficients determined by the two methods is fairly good. The *p*H and potential used for the polarographic determinations are listed for each sulfone.

In early work with sulfone IVa by the polarographic technique, determinations were made in the alkaline region at *p*H 9.2. At this *p*H, sulfone IVa showed a single apparently six-electron reduction wave with a half-wave potential about −0.72 v. (*vs.* S.C.E.) while sulfinic acid VIa showed two waves: one with half-wave potential at about −0.81 v. and the other at about −1.08 v., apparently corresponding to two and four electron reductions, respectively. Currents were measured at a potential (for example, −0.95 v.) on the plateau between the two waves for reduction of VIa, and rate coefficients were derived from them in the usual way. Two runs by this technique are listed in Table I. Determinations in the alkaline region are obviously not suitable for work with the very fast-reacting sulfones, and difficulties were encountered even with other sulfones of type IV.

**General Methods.**—Dioxane was purified by the method of Beste and Hammett,[10] and for determinations by the polarographic method was used within two weeks of purification. Thermostats were constant to ±0.02° except the one at 67.2° which varied by ±0.2°. An automatic recording polarograph (Leeds and Northrup Electrochemograph type E) was used.

The Arrhenius activation energy, $\Delta E$, and the entropy of activation, $\Delta S^\ddagger$, were calculated from standard expressions.[11]

## Results and Discussion

Our rate measurements are summarized in Table II. All the sulfones lacking a 6-substituent (IVa, IVb, IVc, IVd and XIX) rearranged comparatively slowly at 46°, and all those with a 6-substituent (Vb, Vc, Vd and XVb) rearranged with great speed at 0°. Electron-releasing 6-methyl groups and electron-attracting 6-bromo and 6-chloro groups all caused tremendous acceleration of similar magnitude. Therefore the cause of the acceleration is steric and not electronic. It is the size of the 6-substituent and not its electronic effect which is responsible for the great increases in rearrangement rate. Thus the earlier interpretation,[4] which ascribed the acceleration to the electronic effect of 6-methyl groups, is no longer tenable[12] and the view that the acceleration is of steric origin[6] is upheld.

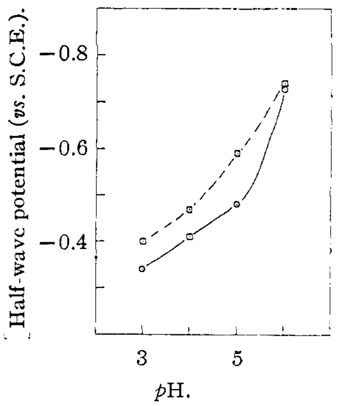

Fig. 2.—Typical variation of reduction potential with *p*H for a 6-substituted sulfone and the related sulfinic acid: solid line, sulfone Vc; broken line, sulfinic acid VIIc.

TABLE II

SUMMARY OF KINETICS DATA

| Sulfone | Substituents[a] | Mean rate coefficient, min.$^{-1}$ At 0.0° | At 46.0° | $\Delta E$, kcal. mole$^{-1}$ | $\Delta S^\ddagger$, e.u. |
|---|---|---|---|---|---|
| IVa | 5-$CH_3$ | | $1.94 \times 10^{-2}$ | 23.8 | −2.0 |
| IVb | 4,5-di-$CH_3$ | $(3.6 \times 10^{-5})$[b] | $1.66 \times 10^{-2}$ | 23.2 | −4.2 |
| Vb | 5,6-di-$CH_3$ | >3 | | | |
| IVc | 4-Cl-5-$CH_3$ | $(1.8 \times 10^{-6})$[b] | $1.44 \times 10^{-3}$ | 25.3 | −2.6 |
| Vc | 6-Cl-5-$CH_3$ | $9.2 \times 10^{-1}$ | | | |
| IVd | 4-Br-5-$CH_3$ | | $1.23 \times 10^{-3}$ | | |
| Vd | 6-Br-5-$CH_3$ | 2.1 | | | |
| XIX | 3-Cl-4,5-di-$CH_3$ | $(7.4 \times 10^{-7})$[b] | $1.0 \times 10^{-3}$ | 27.2 | 2.6 |
| XVb | 3-Cl-5,6-di-$CH_3$ | $1.29 \times 10^{-1}$ | | 20.2 | 1.5 |

[a] A 2-hydroxy and a 2′-nitro group are constant features in all these sulfones. [b] Extrapolated from measurements at higher temperatures.

Before considering the steric effect further, let us look at electronic effects on the rearrangement as revealed by our data. From theory and from experiments by Smiles and his associates, we should expect an ambiguity of electronic effects: the rearrangement should be assisted by electron accession to the ionized hydroxy group and by electron withdrawal from the sulfone bridge. Rearrangement may be retarded by an electron-releasing group which happens to interact more strongly with the sulfone bridge than with the ionized hydroxy group, or by an electron-attracting group which affects the ionized hydroxy group the more powerfully. We have observed just this case: the reaction is retarded by a methyl group or by a halogen atom in the 4-position. The methyl group releases electrons less efficiently to a *meta* than to the *para* position, and thereby affects the reaction rate

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[10] G. W. Beste and L. P. Hammett, THIS JOURNAL, **62**, 2481 (1940).

[11] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

[12] The late Professor Smiles examined a draft of Bunnett and Zahler's chapter on the Smiles rearrangement prior to its publication, and he commented in a letter dated January 3, 1951: ". . . . I do think that the stereochemical aspect of the process which you have introduced is a valuable improvement; it seems to me a logical development and it certainly explains data which seem otherwise unintelligible." Thus there was not any dispute between us and Professor Smiles personally, and our criticism of one small aspect of his published work does not lessen our respect for his many contributions to knowledge of the rearrangement which bears his name.

primarily by its effect on the sulfone bridge. Halogen atoms withdraw electrons from all positions; their effect on the ionized hydroxy group is evidently more important, for they cause the rearrangement rate to decrease about tenfold (compare IVc and IVd with IVa). Chlorine in the 3-position causes a similar decrease (compare XIX with IVb). The electronic effects are interesting, but they are small compared to the steric effects of 6-substituents.

Since the electronic effect of a 6-substituent should be similar to that of the same substituent in the 4-position, the magnitude of the steric acceleration is best judged by comparing the rates of rearrangement of isomeric 4- and 6-substituted sulfones. In the present work, rates at 0° are compared: directly measured rates for 6-substituted sulfones and extrapolated rates for their 4-substituted isomers. Owing to the lack of high precision in the polarographic rate measurements, the extrapolated rates for IVc and XIX should be considered correct only as to their order of magnitude. Also, sulfone Vb rearranged so fast that we can only set a minimum rate coefficient.[13] Therefore, these comparisons can reveal no more than the order of magnitude of the accelerating effect.

From comparison of rates for IVc and Vc at 0°, the 6-chloro group is judged to cause a 500,000-fold acceleration owing to its steric effect. From the rates for XIX and XVb, the steric acceleration caused by a 6-methyl is estimated to be 200,000-fold. And from comparison of rates for IVb and Vb, the acceleration caused by 6-methyl is estimated as at least 100,000-fold, and probably more like 1,000,000-fold. The differences between these estimates cannot be regarded as significant. Their agreement as to order of magnitude is satisfying, in view of the fact that methyl and chloro substituents appear, from other studies,[14] to have similar bulk. The acceleration caused by a 6-chloro or 6-methyl group is thus on the order of $10^5$- to $10^6$-fold, a truly colossal effect. The effect of bromine in the 6-position appears to be of similar magnitude.

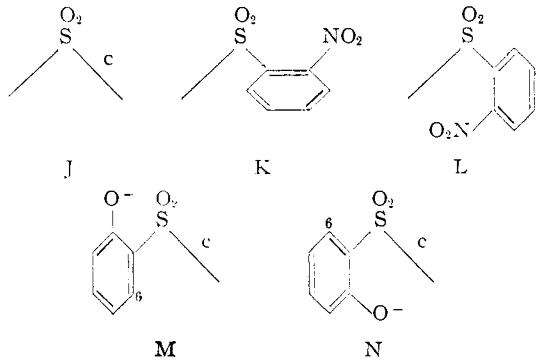

Fig. 3.—Conformation of 2-hydroxy-2′-nitrodiphenyl sulfones.

Owing to the lack of high precision in the polarographic rate measurements, the energies and entropies of activation for IVc, XIX and XVb have a rather large degree of uncertainty. Nevertheless, it seems clear that the entropy of activation is close to zero for all the rearrangements studied and that changes in rate, owing both to electronic and steric effects, arise principally from changes in the energy of activation.

Bunnett and Zahler[6] interpreted the accelerating effect of 6-methyl groups with reference to five extreme conformations for a 2-hydroxy-2′-nitrodiphenyl sulfone molecule. The disposition of bonds about the sulfur atom in a sulfone is approximately tetrahedral,[15] and the various conformations differ from each other by rotation of the phenyl groups about carbon–sulfur bonds. The five extreme conformations are represented in Fig. 3, in which benzene rings which are viewed edgewise are represented by a line and those which present their broad side to our line of view are drawn in the usual way. The small *c* indicates the position of the 1′-carbon atom which must be attacked by the ionized hydroxy group in order for the rearrangement to occur.

Bunnett and Zahler pointed out that conformations resembling N, in which the ionized hydroxy group is brought laterally against the 1′-carbon atom, are prerequisite to reaction. They explained that conformation L involves a great deal of strain between the nitro group and the carbon atoms of the other ring, and is therefore most disfavored. When a large 6-substituent is introduced, conformations resembling M are also rendered improbable, and the probability of the molecular conformation being such as can lead to rearrangement is thereby increased. The result is an increased rate of rearrangement, they explained.

This interpretation is acceptable in broad outline, but it requires some refinement. The enormity of the effect and the fact that in the one case (XVb *vs.* XIX) for which data are available the acceleration arose principally from a change in the energy of activation, show that the introduction of a 6-substituent radically changes the energy required for the activation process. *A priori*, it could either decrease the enthalpy of the transition state or increase that of the initial state or both. Since in the transition state (which is geometrically similar to conformation N) the 6-substituent is in an open and relatively uncrowded situation, it is unlikely that the enthalpy of the transition state is greatly dependent on the bulk of a 6-substituent. Therefore a 6-substituent must change the energy of activation mainly by increasing the enthalpy of the unrearranged sulfone anions.

It is necessary to take account of steric repulsions between the solvated ionized hydroxy group and the carbon atoms of the other ring in conformations of type N. These are probably considerable, and raise the energy of such conformations substantially. Repulsions between the ionized hy-

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(13) It is characteristic of all the sulfones that they take on a reddish hue in alkaline solution, a coloration which fades to pale yellow as the sulfinic acid is formed. In the case of Vb, the reddish hue could be observed briefly at 0° but it faded within a few seconds to light yellow. We conservatively estimate the rate coefficient to be greater than 3 min.$^{-1}$, but we believe it is probably on the order of ten times this value.

(14) R. L. Shriner and R. Adams, in Gilman's "Organic Chemistry," Vol. I, second ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 362; R. W. Taft, THIS JOURNAL, **74**, 3123 (1952).

(15) C. Keil and K. Plieth, *Z. Krist.*, **106**, 388 (1955), found by X-ray crystallographic examination of 4,4′-diiododiphenyl sulfone the following angles: O–S–O, 111 ± 4°; C–S–C, 106 ± 2°.

droxy group and the oxygen atoms of the sulfone bridge probably disfavor conformations resembling J and K too, but to a lesser extent. The solvated ionized hydroxy group is most free in conformations of type M. The less strained conformations are energetically favored and the more heavily populated. In order to rearrange, the molecule must rotate from various "non-rearranging" conformations, especially of type M, into "rearranging" conformations of type N, forcing the solvated ionized hydroxy group into a crowded situation against a significant energy differential.

Now when a large 6-substituent is introduced, conformations of type M are strongly disfavored because of steric compressions between the 6-substituent and the carbon atoms of the other ring, conformations of types J and K are disfavored to a lesser extent because of crowding of the 6-substituent with the oxygen atoms of the sulfone bridge, and "rearranging" conformations like N are rendered most favorable insofar as compressions with the 6-substituent are considered. A new energy differential in favor of the "rearranging" conformations is superimposed on the former differential against them. There is a net decrease in the energy differential between "rearranging" and "non-rearranging" conformations, a consequent decrease in the energy of activation, and therefore a higher rate of rearrangement.

**Acknowledgments.**—Mr. Kenneth M. Pruitt determined many of the titrimetric rate coefficients for sulfones IVa and IVb. We sincerely appreciate his help. Dr. Charles N. Reilley suggested the polarographic method of analysis, and we are grateful to him and to Dr. Rudolf Schmid for advice in connection with its use. We thank the Office of Ordnance Research, U. S. Army, for financial assistance.

CHAPEL HILL, N. C.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

# Sulfonation of Olefins. VII. Sulfonation of 1,1-Diphenyl-2-methyl-1-propene

BY F. G. BORDWELL AND G. W. CROSBY[1]

RECEIVED JUNE 7, 1956

Sulfonation with the dioxane–sulfur trioxide complex was observed to occur at a much slower rate with 1,1-diphenyl-2-methyl-1-propene than with styrenes previously studied. Attack occurred in the aromatic nuclei of the substituted styrene rather than in the side chain. Speculation concerning the significance of these results with regard to the mechanism of sulfonation is given. 2-Chloroethyl chlorosulfonate and 2-chloroethyl hydrogen sulfate were identified as products of the reaction of sulfur trioxide with ethylene chloride.

The previous investigations on the sulfonation of olefins with dioxane–sulfur trioxide complex[2] indicate a prominent role in the reaction for a $\beta$-sultone intermediate. Hydrolysis of this intermediate on addition of water is believed to be the primary source of the $\beta$-hydroxyalkanesulfonic acids formed from equimolar quantities of olefin and sulfonating reagent. The unsaturated sulfonic acids obtained (after hydrolysis) in these reactions also are probably formed, at least in part, from this intermediate.[3] Sulfonation of 1,1-diphenyl-2-methyl-1-propene (I) is of interest in this latter regard, since the expected $\beta$-sultone intermediate II should be rapidly hydrolyzed, but cannot give unsaturated products, unless hydrolysis is accompanied by rearrangement.

The rate of sulfonation of I with a solution of the dioxane–sulfur trioxide complex in ethylene chloride at 0° was found to be much slower than that of styrene. Whereas the reaction with styrene was 60% complete within one minute,[4] that with I was only about 25% complete after 15 hours at 0°, judging from the quantity of sulfuric acid obtained on hydrolysis.

In order to effect sulfonation a solution containing equimolar quantities of I and the sulfonating agent was allowed to stand at room temperature for 15 hours. Under these conditions about 50% of a monosulfonic acid III and 30% of a disulfonic acid IV were formed, judging from the quantities of barium salts isolated. The barium disulfonate was contaminated by 10% or more of sulfonation products resulting from reaction of sulfur trioxide with dioxane. About 5% of the sulfur trioxide was recovered as sulfate, and about 5% was converted to a sultone V.

The products of the sulfonation were isolated by hydrolysis and conversion of the acids present in the aqueous layer to barium salts with barium carbonate. The barium salt of the monosulfonic acid III was soluble in water only to the extent of about 1% by weight, and was separated readily from the more soluble barium salt of the disulfonic acid IV. On oxidation with aqueous potassium permanganate the salts of both III and IV gave acetone, which was identified through its 2,4-dinitrophenylhydrazone. Analysis of distillates from the oxidation mixtures for acetone using the iodine–thiosulfate method of Messinger[5] showed the formation of 68% of acetone from the monosulfonic acid and 44% of acetone from the disulfonic acid under these conditions. These results showed conclusively that sulfonation had occurred in the benzene nucleus rather than in the side chain of

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[1] Winthrop–Stearns Chemical Co. Fellow, 1946–1947; Allied Chemical and Dye Corp. Fellow, 1947–1948. Abstracted from the Ph.D. dissertation of G. W. Crosby, Northwestern University, June, 1949.

[2] See Paper VI in this series, F. G. Bordwell and M. L. Peterson, THIS JOURNAL, **76**, 3957 (1954), for leading references.

[3] This point will be discussed in a later paper in this series.

[4] F. G. Bordwell, M. L. Peterson and C. S. Rondestvedt, THIS JOURNAL, **76**, 3945 (1954).

[5] L. F. Goodwin, *ibid.*, **42**, 39 (1920).