described before, melted at 147–148°, after crystallization from methanol. Admixture with the same derivative of the sulfinic acid obtained by the rearrangement of phenyl 2,4-xylyl sulfone did not depress the melting point.

Anal. Calcd. for $C_{14}H_{13}ClHg$: Cl, 8.53. Found: Cl, 8.51, 8.80.

Acknowledgment.—We wish to acknowledge gratefully the support of this work by the National Science Foundation and by the Union Carbide and Carbon Chemicals Co.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Rearrangements of Aryl Sulfones. III. The Kinetics of the Reaction of *o*-Methyldiaryl Sulfones with *n*-Butyllithium[1]

BY WILLIAM E. TRUCE AND WILLIAM J. RAY, JR.

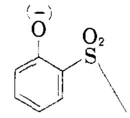
RECEIVED JUNE 2, 1958

A marked difference in the kinetics of the reaction of phenyl *o*-tolyl- and phenyl 2,6-xylyl-type sulfones was observed. This difference is attributed to the steric influence of the 6-methyl group on the latter reaction.

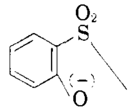
Introduction

In 1937, McClement and Smiles[2] reported that the rate of the base-induced rearrangement of 2-hydroxy-2′-nitrodiphenyl sulfones was accelerated by a methyl group in the 6-position. This acceleration was attributed by them to the electron-releasing ability of the methyl group. Bunnett and Zahler,[3] however, later pointed out that this acceleration can best be explained as the result of a steric rather than an electronic effect, and Bunnett and Okamoto[4] recently have presented convincing evidence in support of this view. These workers found that chloro and bromo as well as methyl substituents in the 6-position exerted a tremendous accelerating effect on the reaction, their presence increasing the first-order rate constant of the rearrangement by as much as 500,000-fold over that of the unsubstituted sulfone. Since the electronically opposite halo and methyl substituents produced a similar accelerating effect on the rearrangement, this effect was taken to be steric in nature and a consequence of the size of the substituent.

These workers also showed that the entropy of activation in all cases examined approached zero and that, "... the changes in rate, owing both to electronic and steric effects, arise principally from changes in the energy of activation."[4] They also reasoned that, "Since in the transition state...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."[4] This change in enthalpy is explained as the result of steric factors which favor conformations similar to M over those similar to N in sulfones lacking a 6-substituent, while favoring conformations such as N over those such as M when a bulky 6-substituent is present. The enthalpy of the favored conformations in the latter case must be substantially greater than the enthalpy of the favored conformations in the former case due to "...steric repulsions between the solvated ionized hydroxyl group and the carbon atoms of the other ring...."[4] Since the rearrangement occurs from conformations such as N, there will be a net difference between the energy required for the rearrangement of these two classes of sulfones equal to the energy necessary to bring about the transformation M→N, prior to rearrangement, in sulfones lacking a bulky 6-substituent.



M

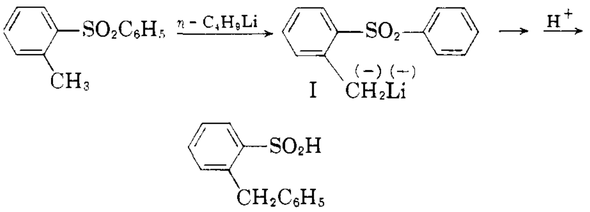


N

With this in mind, it was of interest to examine the kinetics of the related rearrangement of *o*-methyldiaryl sulfones described in parts I[5a] and II[5b] of this series. Of special interest was the fact that in sulfones such as mesityl phenyl sulfone, the two *o*-substituents are of the same size and both are possible sites for metalation and subsequent rearrangement.

Results and Discussion

A mechanism has been postulated for the reaction of *o*-methyldiaryl sulfones with *n*-butyllithium[5a]



If the metalation reaction is rate determining, the over-all reaction rate should be proportional to the sulfone concentration, other variables remaining constant. That this is contrary to fact is indicated by the rate studies involving mesityl phenyl, phenyl 2,4-xylyl and phenyl *o*-tolyl sulfones, the results of which are summarized in Table I.

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[1] Abstracted from Ph.D. thesis of W. J. Ray, Jr.

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

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

[4] J. F. Bunnett and T. Okamoto, THIS JOURNAL, **78**, 5363 (1956).

[5] (a) W. E. Truce, W. J. Ray, Jr., O. L. Norman and D. B. Eickemeyer, *ibid.*, **80**, 3625 (1958); (b) W. E. Truce and W. J. Ray, Jr., *ibid.*, **81**, 481 (1959).

TABLE I

RATE CONSTANTS FOR REARRANGEMENT OF *o*-METHYLDIARYL SULFONES

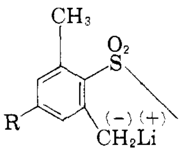
Sulfone	Moles of sulfone per mole of *n*-butyllithium	k, min.$^{-1}$	Average k	Relative rate
Phenyl 2,6-xylyl	1.00	0.306[a]	0.31	82
	1.00	.315[a]		
Mesityl phenyl	0.98	.259[a]	.26	68
	.97	.239[a]		
	1.96	.268[a]		
Phenyl 2,4-xylyl	0.98	.0231	.025	7
	.98	.0243		
	.98	.0251		
	1.96	.0274		
Phenyl *o*-tolyl	1.00	.0187	.018	5
	1.00	.0175		
	2.00	.0184		
Mesityl	1.00	.00378[a]	.0038	1

[a] Applies to the second stage of the rearrangement, for which see the foregoing discussion.

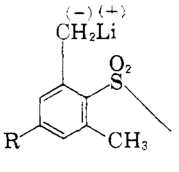
The independence of the over-all reaction rate from the rate of metalation was further substantiated for each sulfone examined by the first-order kinetics of the over-all reaction. The rearrangement of *o*-methyldiaryl sulfones is therefore quite analogous to the Smiles rearrangement of 2-hydroxy-2′-nitrodiphenyl sulfones and parallel effects in the two rearrangements may well be expected from like structural changes in the parent sulfones.

For the purposes of this discussion, the sulfones whose rearrangement rates were investigated are divided into two classes. The first class includes *o*-tolyl-type sulfones, those sulfones having a single *o*-methyl substituent, *i.e.*, phenyl *o*-tolyl sulfone and phenyl 2,4-xylyl sulfone. The second class includes those sulfones having two *o*-substituents in the same ring, or 2,6-xylyl-type, *i.e.*, mesityl phenyl and phenyl 2,6-xylyl sulfones. The rearrangement of both of the sulfones in the *o*-tolyl-type class was strictly first order while the rearrangement of the 2,6-xylyl type sulfones occurred in two stages, the first stage, which accounted for 20 to 25% of the over-all rearrangement, being much too fast to measure at 35° with our apparatus. The rate of the second stage of the reaction was measured, however, and this stage proved to be first order.

Since the two-stage reaction occurred only with sulfones containing the 2,6-xylyl-type group, it seems that the dual-stage character of the reaction is somehow related to the second *o*-methyl group present in these compounds. Thus, if the rotation of the 2,6-xylyl-type group about the carbon–sulfur bond in these sulfones is somewhat restricted, metalation could produce two different intermediates, II and III, which are not freely interconvertible. (Here, as in M and N, the benzene rings which are viewed edgewise are represented by a line and those which present their broadside to the reader's line of vision are drawn in the usual way.) The rearrangement of II should proceed directly because of the favorable geometric relationship between the nucleophilic group and the rearrangement site, while III would need to be converted to II by means of rotation about the carbon–sulfur bond of the xylyl group, before rearranging, since III is not geometrically suited to rearrangement. The rearrangement of II, then, would represent the first stage of the over-all rearrangement of 2,6-xylyl-type sulfones.[6]

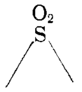


II



III

R = –H, –CH₃



IV

Following this reasoning, the second stage of the rearrangement would be the rate-controlling conversion of III to II followed by a rapid rearrangement of II as in the first stage. The similarity of the rate constants for the second stage of the rearrangement of mesityl phenyl and phenyl 2,6-xylyl sulfones, 0.26 and 0.31, respectively, is consistent with this explanation since these two sulfones are identical with respect to the four *o*-substituents. The rate of conversion of III to II would of course be influenced primarily by the effective size of the *o*-substituents. The *p*-methyl group of the former sulfone would not be expected to appreciably influence the reaction rate.

If this is true, one might then expect mesityl sulfone to rearrange in two stages, also. The first stage should be rapid as in the cases of mesityl phenyl and phenyl 2,6-xylyl sulfones. The second stage, however, should be much slower since the two *o*-hydrogens of those sulfones have been replaced by methyl groups in mesityl sulfone. Such a change should increase the energy required for the rotational conversion III → II (*via* IV). Molecular models indeed indicate that particularly in mesityl sulfone the transition state IV probably would be strained. (The presence of the *p*-methyl group in mesityl sulfone attached to the ring undergoing substitution would not be expected to greatly influence the rearrangement of this sulfone as compared to mesityl phenyl sulfone.) The rearrangement of mesityl sulfone did indeed occur in two stages. The first stage, representing 26% of the over-all reaction, was complete within 25 to 30 seconds,[7] as was the case with mesityl phenyl and phenyl 2,6-xylyl sulfones. The second stage of the rearrangement of mesityl sulfone, however, was only about 0.014 as fast as the second stage of the rearrangement of those sulfones. The assumption that the rate-controlling step in the second stage of the rearrangement of 2,6-xylyl-type sulfones is the rotational transformation III → II is thus in agreement with experiment.

The rearrangement of phenyl *o*-tolyl and phenyl 2,4-xylyl sulfones is first order and occurs in a single

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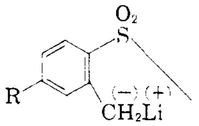
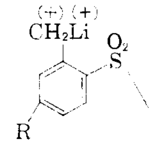
[6] This explanation for the two-stage character of the rearrangement is somewhat weakened by the observation that although immediate carbonation of the metalated reaction mixture from mesityl phenyl sulfone gave an acid with the expected neutral equivalent (arising from III), the material balance was poor.

[7] The rate may actually be much faster than this indicates, 25 to 30 seconds merely representing the time required to mix the reagents and withdraw the first aliquot.

stage. This probably means that the rotation of the *o*-tolyl-type ring about the carbon–sulfur bond is sufficiently less restricted than the rotation of the 2,6-xylyl-type ring so that V and VI are readily interconvertible. In spite of this, however, a comparison of the rates of rearrangement of phenyl *o*-tolyl and phenyl 2,4-xylyl sulfones with those of mesityl phenyl and phenyl 2,6-xylyl sulfones indicates that the former pair rearranges considerably more slowly than the latter pair. Thus, although the energy requirement for the rotational conversion of the non-rearranging form VI to the rearranging form V of these sulfones is almost certainly less than that for the conversion of III to II in the case of 2,6-xylyl-type sulfones, the over-all energy requirement for the reaction (IV$\rightleftarrows$V)$\rightarrow$ Ar'SO_2Li apparently is greater than that for III $\rightarrow$ II $\rightarrow$ $ArSO_2Li$. The rate-controlling step in the rearrangement of the phenyl *o*-tolyl-type sulfones, then, cannot be the rotational transformation VI$\rightarrow$ V, but must be the actual rearrangement step, V $\rightarrow$ Ar'SO_2Li. This rearrangement, then, must be considerably slower than the corresponding step II $\rightarrow$ $ArSO_2Li$ in the case of the 2,6-xylyl-type sulfones. Although we were unable to measure the rate of the initial rearrangement step, II$\rightarrow$ $ArSO_2Li$, of any of the three phenyl 2,6-xylyl-type sulfones, a lower limit for the rate constant of this step may be estimated for comparison with the rate constant of the rearrangement step, V$\rightarrow$ $ArSO_2Li$, of the phenyl *o*-tolyl-type sulfones. With each of the phenyl 2,6-xylyl-type sulfones, this first stage of the rearrangement was complete, within experimental error, in 25 to 30 seconds.[7] Assuming the reaction was 90% complete at this time, the rate of the reaction II$\rightarrow$$ArSO_2Li$ must then be at least 200 times faster than that of V $\rightarrow$ Ar'SO_2Li.



V, R = –H, –CH_3



VI, R = –H, –CH_3

That II should rearrange much faster than V, although it differs from V by a single 6-methyl group, is not surprising in view of the recent work of Bunnett and Okamoto[4] referred to earlier. Apparently the same type of steric effect described by those workers is operative here. Thus the 6-methyl group might well enhance the rate of rearrangement of II by increasing its enthalpy, as compared to V, while having little effect on the enthalpy of the respective transition states. Or, in other words, the enhancement can easily be explained as the result of steric strain in II which is relieved in the transition state. Such strain might involve repulsions between the 6-methyl group and the sulfone oxygens resulting in a decrease of the C–S–C bond angle of II relative to V. This would force the $\overset{(-)(+)}{-CH_2Li}$ group of II nearer to the face of the opposing benzene ring and thus into a position of higher energy.

The explanation here advanced regarding the rearrangement of 2,6-xylyl-type sulfones suggests that properly substituted derivatives of such sulfones, particularly mesityl sulfone, might be capable of optical isomerism similar to that encountered in hindered biphenyl derivatives, owing to the restricted rotation of the 2,6-xylyl or mesityl groups about the carbon sulfur bond. Optical activity has not heretofore been observed in such sulfones; one unsuccessful attempt[8] to resolve a derivative of mesityl sulfone has been reported.

Experimental

The Reaction of *o*-Methyldiaryl Sulfones with *n*-Butyllithium: Rate Studies.—A 1000-ml., 3-neck flask equipped with a mechanical stirrer and a water condenser was used for all rate studies. A large, Dry Ice condenser was attached to the water condenser, and vented to the atmosphere *via* a U-tube. A short section of 12-mm. Pyrex tubing was sealed to the flask to act as a nitrogen inlet. The flask also was equipped with a 10-ml., buret-type sample remover constructed from a 3-way stopcock (stopcock I). One arm of this stopcock was extended into the flask almost to the bottom. To the second arm, extending vertically from the flask, was attached a bulb so that this arm resembled a short pipet. Graduations indicating volumes of 0.1 ml. were placed on each side of the 10-ml. mark above the bulb. The buret could be exhausted through the third arm of the stopcock.

Nitrogen was introduced into the system *via* a 3-way stopcock (stopcock II) through either the nitrogen inlet or the top of the sample buret. Between stopcock II and the buret was placed a T-tube which was vented to the atmosphere *via* a U-tube.

Before each reaction, the apparatus was thoroughly dried at 110° and assembled while still hot. After introducing the sulfone,[9] the system was flushed with a slow stream of nitrogen overnight. When flushing was complete, the Dry Ice condenser was filled and 600 ml. of anhydrous ether introduced into the flask. A very slow stream of nitrogen was used from this point on except when taking samples. The solution was heated almost to reflux and the mechanical stirrer started. To the refluxing solution was added, rapidly, the required amount of *n*-butyllithium *via* a buret. The organometallic was prepared and standardized by the method of Jones and Gilman.[10] The addition was carried out *via* the nitrogen inlet, the nitrogen connection being broken momentarily to allow this.

During the run, stopcock I remained closed except when samples were taken. To take an aliquot, this stopcock was turned so that the flask was connected to the sampling buret and the flow of nitrogen was increased sharply. At the same time, the nitrogen vent was closed, thus forcing the reaction mixture into the sampling buret. When the buret had been filled to the mark, stopcock I was closed and the nitrogen vent opened. After the volume of the solution in the buret was noted, the contents were exhausted by opening stopcock I and turning stopcock II so that nitrogen entered the top of the buret. Using such a procedure, three 10-ml. aliquots accurate to 0.1 ml. could be taken each minute under a nitrogen atmosphere.

The aliquots were run into 50-ml. beakers containing 1 ml. of methanol. After the ether was evaporated with air, 15 ml. of water was added and each aliquot neutralized to phenolphthalein with dilute acid. The analysis utilized the insolubility of ferric sulfinates described by Krishna and Singh.[11] Thus, to the neutral solution was added 10 ml. of a standard iron solution containing 1.80 g. of ferric chloride hexahydrate and 5 ml. of concentrated hydrochloric acid per liter. The beakers then were covered with watch glasses and heated for 25 minutes on a steam-plate. The insoluble ferric sulfinate in each aliquot was filtered off using a sintered glass, büchner-type funnel of medium porosity. The filtrate was diluted to 100 ml. and a 10-ml. aliquot analyzed colorimetrically for residual ferric ion using a method similar to

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[8] M. E. Maclean and R. Adams, THIS JOURNAL, **55**, 4685 (1933).

[9] Fifteen millimoles of sulfone was used except where the effect on the rate of increasing the sulfone concentration was studied: see Table I.

[10] R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339.

[11] S. Krishna and H. Singh, THIS JOURNAL, **50**, 792 (1928).

that described by Fortune and Mellon.[12] Thus, to each aliquot was added 0.5 ml. of 15% hydrochloric acid, 2 ml. of 15% hydroxylamine hydrochloride, 10 ml. of a saturated sodium acetate solution and 10 ml. of 0.1% α-phenanthroline solution. The resulting red solution was diluted to 100 ml. and the color intensity measured in a round absorption cell approximately 22 mm. in diameter. A Fisher electrophotometer equipped with a green filter, λ_{max} approximately 525 mμ, was used for the color measurements. The difference between the absorption with and without added sulfinic acid is a measure of the precipitated ferric sulfinate which may be related to the amount of added sulfinic acid. The analysis was calibrated for each sulfinic acid by analyzing various aliquots of a standard solution of that acid[5,6] in the same manner as above. The first-order rate constants for the rearrangement of each of the sulfones listed in Table I were determined by plotting ln (100 − % reaction) *vs.* time in minutes. The slopes of the resulting straight lines were determined by the method of least squares and the rate constants so calculated are shown in Table I together with the number of runs for each sulfone. Except for phenyl 2,4-xylyl sulfone, 10 to 12 points were taken during each run and the run was carried to within 70–85% completion. With phenyl 2,4-xylyl sulfone, 15 points were taken up to 60 to 70% completion. Since the conversion with phenyl *o*-tolyl and phenyl 2,4-xylyl sulfones was only about 60%,[6] the analysis gave somewhat less satisfactory results than with the other sulfones, the standard deviation of a single measurement being about 5%. For the other sulfones this value was about 3%. The standard deviation of rate constants from successive runs was generally slightly greater than the above values but was not greater than 7%.

For mesityl phenyl, phenyl 2,6-xylyl and mesityl sulfones, the first-order plot gave a straight line which did not pass through the origin on extrapolation. The extrapolated link intersected the ordinate at a point representing the percentage of the over-all reaction accounted for by the first stage, for which see the Discussion. The "% reaction" which was plotted for these sulfones represents the fraction of the reaction in excess of this first stage.

Acknowledgment.—We wish to gratefully acknowledge the support of this work by the National Science Foundation and the Union Carbide and Carbon Chemicals Co.

Lafayette, Ind.

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[12] W. B. Fortune and M. G. Mellon, *Anal. Chem.*, **10**, 60 (1938).

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

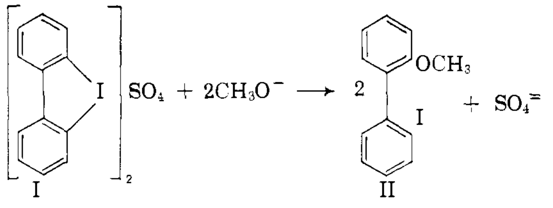
Synthesis of 2-Iodo-2′-Methoxybiphenyl. A New Route to *o*-Terphenyls[1]

By Reynold C. Fuson and Robert L. Albright[2]

Received August 21, 1958

2-Iodo-2′-methoxybiphenyl has been prepared from biphenyleneiodonium sulfate by a three-step transformation. 2-Acetoxy-2′-iodobiphenyl, obtained by the action of sodium acetate on the iodonium sulfate, underwent methanolysis to give the corresponding phenol. Finally, the desired iodo methyl ether was produced by methylation of the phenol with methyl sulfate. The transformation was nearly quantitative at each step. The Grignard reagents made from 2-iodobiphenyl and 2-iodo-2′-methoxybiphenyl were condensed with duryl *o*-methoxyphenyl ketone to give the corresponding *o*-terphenyl derivatives. Carbonation of the Grignard reagent from the methoxy iodide yielded 2′-methoxy-2-biphenylcarboxylic acid.

In connection with a study of Grignard reagents containing ether functions[3] attention was directed to the reagents corresponding to the 2-halo-2′-alkoxybiphenyls. It was hoped that the iodo ethers of this series could be made by the action of alkoxide ions on biphenyleneiodonium salts. The iodonium salts had been made available by adaptation of the method of Beringer, Drexler, Gindler and Lumpkin[4] to 2-iodobiphenyl.[5] The first experiments designed to this end involved treatment of biphenyleneiodonium sulfate (I) with sodium methoxide.

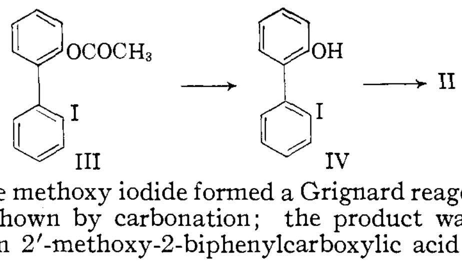


By analogy with similar experiments in the diaryliodonium series[6] it seemed possible that sodium methoxide might bring about displacement to give 2-iodo-2′-methoxybiphenyl (II).

It soon became evident that nucleophilic displacement with methoxide ion in the cyclic iodonium salts was much more difficult to accomplish than in the open-chain analogs. The products were biphenyl, 2-iodobiphenyl and 2,2′-diiodobiphenyl. None of the desired 2-iodo-2′-methoxybiphenyl (II) could be found.

An indirect method was developed, however, by which this compound could be made, the initial step of which was displacement by acetate ion. This reaction, which was carried out in boiling glacial acetic acid, proved to be catalyzed by copper salts. The product, 2-acetoxy-2′-iodobiphenyl (III), was obtained in nearly quantitative yields.

Methanolysis of the iodo acetate gave the corresponding phenol IV, which in turn was methylated to produce the methoxy iodide II. The yields in these steps were very high also.



The methoxy iodide formed a Grignard reagent as was shown by carbonation; the product was the known 2′-methoxy-2-biphenylcarboxylic acid (V).[7]

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[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

[2] Lubrizol Corporation Fellow, 1956–1958.

[3] R. C. Fuson and B. Freedman, *J. Org. Chem.*, **23**, 1161 (1958).

[4] F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, This Journal, **75**, 2705 (1953).

[5] J. Collette, D. McGreer, R. Crawford, F. Chubb and R. B. Sandin, *ibid.*, **78**, 3819 (1956).

[6] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953).

[7] H. G. Rule and E. Bretscher, *J. Chem. Soc.*, 925 (1927).