ment 1. Acetate Va (353 mg., 0.95 mmole), 720 mg. (10 mmoles) of sodium acetate, and 25 ml. of glacial acetic acid were heated at reflux for 1 month. Usual work-up provided 350 mg. of a clear, colorless oil. Analysis of the oil by n.m.r. indicated that it was a mixture of 73% VIa and 27% unchanged Va. This mixture was dissolved in 25 ml. of glacial acetic acid and allowed to react as before for 1 additional month. Work-up and n.m.r. analysis of the product showed a quantitative conversion to 4-thiatribenzotricyclo-[4.3.2.0^{5,9}]undeca-2,7,10-triene (X). Although VIa was produced in this and other experiments, it was not isolated.

Experiment 2. Acetate Va (460 mg., 1.2 mmoles) was warmed on the steam bath in 10 ml. of 0.01 *M* perchloric acid in glacial acetic acid for 20 min. Usual work-up and n.m.r. analysis showed X to be the only product.

Experiment 3. Acetate Va (894 mg., 2.4 mmoles) was dissolved in 35 ml. of 1 *M* perchloric acid in acetic acid. The solution was stirred at room temperature for 3 days and then poured into water. Usual work-up gave 1.2 g. of a clear oil. The oil was crystallized from ethanol yielding 547 mg. (73%) of pure X, m.p. 165–166.5° (cor.).[23] The n.m.r. spectrum of X had the usual complex aromatic absorptions at τ 2.9 (12 protons), an overlapping multiplet at 6.0 (three protons), and a multiplet at 6.9 (one proton). *Anal.*

Calcd. for C$_{22}$H$_{16}$S: C, 84.57; H, 5.16; S, 10.26. Found: C, 84.43; H, 5.19; S, 10.16.

Desulfurization of 4-Thiatribenzotricyclo[4.3.2.0^{5,9}]-undeca-2,7,10-triene (X). The thioether X (0.400 g., 1.3 mmoles) was dissolved in 100 ml. of dioxane containing 20 ml. of water. Raney nickel W-2[25] (15 g.) was added, and the solution was heated at reflux for 23 hr. The nickel sludge was removed by filtration and the filtrate was evaporated with a stream of warm, dry air, leaving a clear oil. The oil was crystallized from ethanol to yield 0.280 g. (78%) of pure *exo*-4-phenyl-dibenzobicyclo[3.2.1]octadiene (XI), m.p. 112–114° (cor.). A mixture melting point of XI with 7-phenyl-dibenzobicyclo[2.2.2]octadiene[26] was depressed.

Epimerization of anti-8-Thiomethoxydibenzobicyclo-[3.2.1]octadiene exo-4-ol Acetate(VIIb) to the endo Isomer VIIIb. Treatment of the *anti–exo* acetate VIIb with 0.1 *M* anhydrous perchloric acid in acetic acid as in the case of the *syn–exo* acetate Va produced an *exo–endo* equilibrium ratio of 6:4. This mixture also did not rearrange back to a bicyclo[2.2.2] derivative on prolonged treatment with 0.1 *M* perchloric acid but decomposed instead. The *endo* isomer VIIIb was not isolated.

Analytical. Nuclear magnetic resonance spectra were obtained using a Varian Associates Model A-60 spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are uncorrected, except where noted.

(23) Although n.m.r. analysis clearly indicated the presence of X as a product in these reactions, an unequivocal proof of its structure was obtained only upon Raney nickel desulfurization (*vide infra*). Furthermore, the n.m.r. spectrum of X was different from that of another possible isomer, 3-thiatribenzotricyclo[5.2.2.0^{2,6}]undeca-4,8,10-triene,[24] which exhibited a complex multiplet at τ 5.8 and a doublet at 6.3 (J = 7 c.p.s.) which had additional fine splitting.
(24) W. Davies and Q. N. Porter, *J. Chem. Soc.*, 459 (1957).

(25) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 181.
(26) W. E. Noland, M. S. Baker, and H. I. Freeman, *J. Am. Chem. Soc.* 78, 2233 (1956).

Sulfenes in the Base-Induced Solvolysis of Alkanesulfonyl Chlorides[1,2]

J. F. King and T. Durst

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada. Received July 22, 1965

The solvolysis of alkanesulfonyl chlorides in various basic media is found to be accompanied by exchange of one and only one hydrogen atom α to the sulfonyl group. In nonbasic media the solvolysis proceeds without α-hydrogen exchange. From a detailed consideration of the possible mechanisms of reaction, it is inferred that the data show that the base-induced reaction takes place through the intermediacy of a sulfene.

In 1911 Wedekind and Schenk[3] suggested that the action of tertiary amines on an aliphatic sulfonyl halide

may lead to a species RR'C=SO$_2$, which they named a "sulfene," by analogy with ketene which had been discovered only a short time before. Subsequent study has lent considerable support to the idea that sulfenes are intermediates in this and other transformations, though none of the work reported before the initiation of this study[4] could be said to have established the point rigorously. These earlier studies have, however, made it possible to describe in some detail the chemical properties which sulfenes must have if, in fact, they do play the role which has been ascribed to them. Of particular relevance to the present discussion is the

(1) Organic Sulfur Mechanisms. II. Reference 4a is to be considered as part 1 in the series.
(2) This work was supported *via* a grant-in-aid and a studentship by the National Research Council of Canada.
(3) E. Wedekind and D. Schenk, *Ber.*, 44, 198 (1911).

(4) The earlier investigations are summarized elsewhere: (a) J. F. King, P. de Mayo, E. Morkved, A.B.M.A. Sattar, and A. Stoessl, *Can. J. Chem.*, 41, 100 (1963); (b) W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, 85, 3231 (1963).

conclusion that sulfenes, if actually formed as hypothesized, must react with water to form the corresponding sulfonic acid, with alcohols to yield the appropriate esters, and with ammonia or primary or secondary amines to give the sulfonamides.

The note of doubtful authenticity associated with sulfenes is betrayed not only by the cautious phraseology guarding most proposals of sulfene participation in a reaction, but also by the number of instances in which a discussion of mechanism is presented but in which even the possibility of a sulfene intermediate is ignored. Particularly striking illustrations of the latter point may be found in a number of reports describing kinetic studies of the hydrolysis of aliphatic sulfonyl halides.[5] In each of these papers some discussion of the mechanism of the reaction is presented, and each (with varying degrees of emphasis) alludes to the notably faster rate of reaction in the presence of base, but the results are interpreted largely in terms of a direct displacement mechanism and in no instance is a sulfene mentioned at all.

The notion that the base-induced solvolysis of alkanesulfonyl halides should be investigated with an eye to detecting the participation of sulfenes, stems, in some measure at least, from an almost trivial observation that we made in the course of re-examining[6] the experiments described by Wedekind.[3] We were struck by the fact that the Wedekind reaction is exceptionally fast, and therefore, if a sulfene is in fact an intermediate, then its formation must be even faster. Such a remarkable ease of formation suggested in turn that sulfenes might be intermediates in other reactions in which their participation had not been hitherto suspected, for example, in the solvolysis of aliphatic sulfonyl halides. This possibility had more than routine interest, because it seemed that the reaction might be sufficiently simple to allow a definite decision on the question of whether or not sulfenes really exist as intermediates in chemical transformations.

The basis of our work lies in the view that if a sulfene is an intermediate in a solvolysis reaction, then this will become readily apparent on using the technique of deuterium labeling. Thus if the hydrolysis of phenylmethanesulfonyl chloride ($PhCH_2SO_2Cl$), for example, were to proceed via phenylsulfene ($PhCH{=}SO_2$), then the acid obtained in the presence of excess deuterium oxide would have one deuterium atom attached to the α carbon; that is, the product would be $PhCHDSO_3D$. With a direct displacement mechanism, on the other hand, the benzylic hydrogens would be unaffected and the product from $PhCH_2SO_2Cl$ would be $PhCH_2SO_3D$. Regardless of what mechanism were to operate, there would exist the hazard that any attempt to apply the distinguishing experiment might be confused by deuterium incorporation from side reactions. In the event, these difficulties did not materialize to any significant extent, as may be seen in the detailed description of the results and the discussion of the mechanism which form the main part of this paper.

(5) (a) R. B. Scott, Jr., and R. E. Lutz, J. Org. Chem., 19, 830 (1954); (b) G. Geiseler and F. Asinger, Chem. Ber., 89, 1100 (1956); (c) H. K. Hall, Jr., J. Am. Chem. Soc., 78, 1450 (1956); (d) R. Foon and A. N. Hambly, Australian J. Chem., 15, 668 (1962).

(6) (a) J. F. King and T. Durst, Tetrahedron Letters, 585 (1963); (b) see also, T. Durst, Ph.D. Thesis, University of Western Ontario, 1964, p. 39 ff.

Shortly after submitting a preliminary report for publication, we learned that a study which was identical in essence though rather less extensive than ours, had been carried out independently by Truce and co-workers, and it was arranged that the two preliminary communications should appear simultaneously.[7,8]

Results

Hydrolysis of Phenylmethanesulfonyl Chloride Catalyzed by Triethylamine. The hydrolysis, when carried out by dissolving phenylmethanesulfonyl chloride in dioxane containing a 50-fold excess of deuterium oxide and treating with a moderate excess of triethylamine, was complete in less than 1 min. at room temperature. The product, triethylammonium phenylmethanesulfonate, was converted to the sulfonyl chloride in order to facilitate physical and chemical analyses.

The following evidence established that the product was almost exclusively phenylmethanesulfonyl-1-*d* chloride ($PhCHDSO_2Cl$). The deuterium analysis corresponded to the presence of an average of 0.977 atoms of deuterium per molecule of sulfonyl chloride. The n.m.r. spectrum showed, in addition to the aromatic absorption at 7.43 p.p.m. only one other signal, a $1:1:1$ triplet ($J = 2.1$ c.p.s.) at 4.83 p.p.m. attributable to the benzylic proton; the areas of the two absorptions were in the ratio 5.0 to 1.04. The coupling constant of 2.1 c.p.s. is in good agreement with previously reported values for geminal H–D couplings.[9] The peaks in the mass spectrum of the natural abundance isomer at m/e 126 (6.90% of Σ_{38}) and m/e 91 (29.5% of Σ_{38}) were shifted to m/e 127 and m/e 92 in the spectrum of the deuterated compound. The intensities of the peaks at m/e 128 and m/e 93 in the spectrum of the deuterated compound were such as to exclude the possibility of more than 2.5% of the dideuterated material ($PhCD_2SO_2Cl$). The amount of deuterium incorporation as estimated from the relative intensities of the peaks at m/e 92 and 91 in the spectrum of the deuterated material agreed within experimental error with the values obtained from deuterium analysis and integration of the n.m.r. spectrum. The infrared spectrum of the monodeuterated compound showed very weak absorption due to C–D stretching at 2220 and 2191 cm.$^{-1}$ and completely lacked the CH_2 bending mode which appeared at 1401 cm.$^{-1}$ in the spectrum of the natural abundance isomer. The second sulfonyl stretching band around 1170 cm.$^{-1}$, which is a strong broad band in the spectrum of the natural abundance isomer, is split into three peaks in that of the monodeuterated phenylmethanesulfonyl chloride. This feature was also observed in all of the other monodeuterated compounds encountered in this study. The three peaks coalesced to a single, strong band at 1175 cm.$^{-1}$ on going from $PhCHDSO_2Cl$ to $PhCD_2SO_2Cl$ (the latter compound was prepared by repetition of the experiment outlined above, see the Experimental Section). Comparison of the infrared spectra of the material from the single reaction with D_2O (*i.e.*, $PhCHDSO_2Cl$) and of the product from the repetitive deuteration experiments ($PhCD_2SO_2Cl$) with the spectrum of the ordinary

(7) J. F. King and T. Durst, J. Am. Chem. Soc., 86, 287 (1964).

(8) W. E. Truce, R. W. Campbell, and J. R. Norell, ibid., 86, 288 (1964).

(9) M. Barfield and D. M. Grant, ibid., 85, 1899 (1963).

sulfonyl chloride ($PhCH_2SO_2Cl$) clearly indicated that none of these materials could contain any more than very small amounts of either of the others.

Finally, as chemical evidence that the deuterium incorporation during the triethylamine hydrolyses occurred only at the benzylic position, a reaction was carried out which was known to remove both benzylic hydrogens and which could be performed without any labile protons being present in the reaction mixture. This was the reaction with triethylamine in cyclohexane which has been shown[6,10] to give a mixture of cis- and trans-oxythiobenzoyl chlorides. When phenylmethanesulfonyl-1,1-d_2 chloride ($PhCD_2SO_2Cl$) was so treated, the product was found, after conversion to the more conveniently crystalline derivative oxythiobenzanilide ($PhCSONHPh$), to be identical in all respects with the natural abundance material, indicating thereby the absence of any deuterium incorporation in the benzene ring.

Alcoholyses of Phenylmethanesulfonyl Chloride Catalyzed by Triethylamine. The triethylamine-catalyzed alcoholyses of phenylmethanesulfonyl chloride were most commonly carried out in the deuterated alcohols. In these cases the products of the reaction, *i.e.*, the phenylmethanesulfonate esters, were examined directly, thereby eliminating any possibility of loss of deuterium in subsequent steps.

When phenylmethanesulfonyl chloride was dissolved in isopropyl alcohol-*d* (92 $\pm$ 2% active deuterium content) and treated with excess triethylamine for 1 min., the isopropyl ester was obtained. The constitution of this material was established in a manner very similar to that used to show the nature of the hydrolysis product. Thus, the melting point of the ester from the above reaction showed no depression on admixture with a sample of natural abundance isopropyl phenylmethanesulfonate, and the average deuterium incorporation was found to be 0.909 atom per molecule, which is to say approximately the same as the deuterium content of the isopropyl alcohol used in the reaction. The peaks in the mass spectrum of the natural abundance isomer at m/e 91 and m/e 107 were largely shifted in the spectrum of the deuterated material to m/e 92 and 108. The intensities of the peaks at m/e 93 and 109 were such as to exclude the possibility of more than 2% dideuterated material. The amount of deuterium incorporation as calculated from the mass spectra agreed well with the value obtained by n.m.r. integration. The infrared spectrum of the monodeuterated material showed the absence of the CH_2 bending mode which appears at 1410 cm.$^{-1}$ in the spectrum of the natural abundance isomer. The single sulfonyl stretching band at 1173 cm.$^{-1}$ in the spectrum of the natural abundance isomer was again changed to three peaks (at 1188, 1175, and 1155 cm.$^{-1}$) in that of the monodeuterated material.

Treatment of isopropyl phenylmethanesulfonate with triethylamine in isopropyl alcohol-*d* for 1 hr. at 50° resulted in the incorporation of 0.146 atom of deuterium per molecule. Exchange under the much milder conditions of the alcoholysis can therefore be expected to be negligible.

The triethylamine-catalyzed methanolysis was carried out (i) in neat methanol-*d*, (ii) in cyclohexane containing

(10) J. F. King and T. Durst, *J. Am. Chem. Soc.*, **85**, 2676 (1963).

a 1 molar excess of methanol-*d*, and (iii) in ether containing an equimolar amount of the deuterated alcohol. In each case, as is shown below, monodeuterated methyl phenylmethanesulfonate ($PhCHDSO_3CH_3$) was the major ether-soluble product obtained.[11] The infrared spectrum of the products of the reaction carried out in cyclohexane and in ether showed no evidence of either oxythiobenzoyl chloride or *trans*-stilbene (*cf.* ref. 6 and 10). The reaction of phenylsulfene with methanol (assuming this to be the mechanism) is therefore much faster than either the coupling reaction or the oxythiobenzoyl chloride formation.

The deuterated methyl ester obtained from the reaction in neat methanol-*d* above was identical with that obtained by treating $PhCD_2SO_2Cl$ with triethylamine in ordinary methanol. Deuterium analysis of this latter sample showed 9.74 atom % excess deuterium, equivalent to the presence of 0.974 atom of deuterium per molecule. The n.m.r. spectrum showed a partially resolved triplet at 4.21 p.p.m. equivalent to one proton in addition to the phenyl and methoxyl protons at 7.35 and 3.67 p.p.m., respectively. The infrared spectrum (see the Experimental Section) also strongly supports the conclusion that the material is methyl phenylmethanesulfonate-1-*d* and clearly precludes the presence of significant amounts of the dideuterated or undeuterated esters.

The final alcoholysis was carried out in deuterated *t*-butyl alcohol which had been prepared from sublimed potassium *t*-butoxide and D_2O. When the reaction mixture was worked up in the same way as the other alcohols, the product obtained was not *t*-butyl phenylmethanesulfonate but rather triethylammonium phenylmethanesulfonate, presumably produced by the solvolysis of the original ester. An oil, whose infrared spectrum was rather similar to that of isopropyl phenylmethanesulfonate, could be isolated when the reaction was carried out in the cold in small quantities (less than 100 mg. of $PhCH_2SO_2Cl$). This would appear to be *t*-butyl phenylmethanesulfonate. No real attempt, however, was made at obtaining a pure sample because of its apparent instability, an observation that is not surprising in view of Hoffmann's report[12] that *t*-butyl *p*-toluenesulfonate decomposed to *p*-toluenesulfonic acid and isobutylene with a half-life of 30 min. at 0°.

An attempt to prepare the *t*-butyl ester in larger quantities was not successful. When several millimoles of phenylmethanesulfonyl chloride were dissolved in *t*-butyl alcohol and treated with excess triethylamine, an oil corresponding to about a 70% yield of *t*-butyl ester could be obtained upon extraction with ice water and ether. Bubbles began to form in the oil when it was left at room temperature for a few minutes. The infrared spectrum after 10 min. showed only phenylmethanesulfonic acid.

The triethylammonium phenylmethanesulfonate obtained when the reaction was carried out in deuterated *t*-butyl alcohol (90 $\pm$ 3% active deuterium content) was converted to phenylmethanesulfonyl chloride by

(11) In the experiments carried out in ether and in cyclohexane, the product contained some undeuterated ester. This probably derives from two sources: (i) dilution of the deuterium isotope by traces of water in the solvent and (ii) further dilution by hydrogen released from starting material as the reaction progresses.
(12) H. M. Hoffmann, *Chem. Ind.* (London), 336 (1963).

treatment with phosphorus pentachloride. The infrared and n.m.r. spectra of the sulfonyl chloride showed it to be phenylmethanesulfonyl-1-d chloride (PhCHDSO$_2$Cl) containing perhaps a little more of the undeuterated material than that obtained from the hydrolysis experiments (as would be expected in view of the lower isotopic purity of the t-butyl alcohol).

Reaction of Phenylmethanesulfonyl Chloride with Other Bases. Hydrolysis of phenylmethanesulfonyl chloride in the presence of pyridine gave pyridinium phenylmethanesulfonate, which was then converted to the phenylmethanesulfonyl chloride. The infrared and n.m.r. spectra of this material were identical with those of the phenylmethanesulfonyl-1-d chloride obtained from the triethylamine-catalyzed hydrolysis of phenylmethanesulfonyl chloride.

The reaction of phenylmethanesulfonyl chloride in D$_2$O containing excess NaOD was complete in less than 2 min. The infrared and n.m.r. spectra of the phenylmethanesulfonyl chloride, obtained by the usual procedure, were again identical with those of phenylmethanesulfonyl-1-d chloride, obtained from the triethylamine-catalyzed hydrolysis.

Diethylamine also reacted very rapidly with the sulfonyl chloride (in this case, phenylmethanesulfonyl-1,1-d_2 chloride, PhCD$_2$SO$_2$Cl). The product, obtained in 93% yield, was shown to be N,N-diethylphenylmethanesulfonamide-1-d (PhCHDSO$_2$NEt$_2$) by comparison of the melting point and mixture melting point with the natural abundance isomer, by the presence of a band at 4.18 p.p.m. equivalent to a single proton in its n.m.r. spectrum, and by deuterium analysis which showed the presence of 1.05 atoms of deuterium per molecule.

The reaction with aniline is slower. In refluxing benzene, PhCD$_2$SO$_2$Cl reacted with aniline to give a 78% yield of the phenylmethanesulfonanilide within 2 hr. The product was again shown to be monodeuterated at the benzylic carbon by deuterium analysis, which showed the presence of 1.06 atoms of deuterium per molecule, and by the appearance of a broadened signal at 4.3 p.p.m. in the n.m.r. spectrum equivalent to a single proton.

The Triethylamine-Catalyzed Hydrolysis of Other Sulfonyl Chlorides. To see if the exchange of one hydrogen atom during base-catalyzed hydrolysis also occurs with compounds other than phenylmethanesulfonyl chloride, we briefly investigated the hydrolysis of methanesulfonyl, ethanesulfonyl, and 2-phenylethanesulfonyl chlorides in the presence of triethylamine. The reaction in each case was complete in less than 10 min., after which time the product was converted by means of phosphorus pentachloride to the sulfonyl chloride, which then was subjected to deuterium analysis and n.m.r. spectrometry.

The ethanesulfonyl chloride so obtained showed the presence of 0.93 atom of deuterium per molecule. The n.m.r. spectrum, however, supplied the most striking proof that the material was almost entirely ethanesulfonyl-1-d chloride (CH$_3$CHDSO$_2$Cl). The spectrum had a doublet of 1:1:1 triplets at 1.62 p.p.m. ($J_{HH \text{ vic}}$ = 7.2 c.p.s., $J_{HD \text{ vic}}$ = 1.1 c.p.s.) due to the methyl group, and a quartet of 1:1:1 triplets at 3.65 p.p.m. ($J_{HD \text{ gem}}$ = 2.2 c.p.s.) arising from the proton on C-1. The relative areas of the two peaks were esti-

mated to be 3:1.1. The spectrum also showed small but clearly detectable peaks due to the presence of a little CH$_3$CH$_2$SO$_2$Cl.

Phenylethanesulfonyl chloride yielded a product which analyzed for the presence of 0.94 atom of deuterium per molecule. The n.m.r. spectrum indicated a ratio of 5:2:1 for the protons of the aromatic ring, C-2, and C-1, respectively.

Deuterium incorporation in the reaction with methanesulfonyl chloride appeared to be somewhat lower than with the other sulfonyl chlorides studied. The deuterium analysis of the product corresponded to the presence of 0.72 atom of deuterium per molecule, and the n.m.r. spectrum indicated a ratio of CH$_2$DSO$_2$Cl to CH$_3$SO$_2$Cl of roughly 4:1.

The Hydrolysis and Methanolysis of Phenylmethanesulfonyl Chloride without Added Base. Further solvolyses were carried out in natural abundance solvents without added base, using phenylmethanesulfonyl-1,1-d_2 chloride as substrate. The sulfonyl chloride was treated with 50% aqueous dioxane at 50° for 90 min. Analysis of the recovered starting material (24%) by infrared spectroscopy showed that no deuterium exchange had taken place. The sulfonic acid formed by hydrolysis was converted in the usual manner to the sulfonyl chloride, which was found to be identical with the starting material.

The methanolysis was carried out in methanol at 50° for 90 min. The infrared spectrum of the recovered sulfonyl chloride (49%) was identical with that of the starting material. The methyl ester, obtained in 35% yield, analyzed for 1.94 atoms of deuterium per molecule; it showed only phenyl and methoxyl hydrogens in the n.m.r. spectrum. These data show the compound to be PhCD$_2$SO$_3$CH$_3$.

The solvolysis reactions in the absence of added base are significantly slower than the triethylamine-catalyzed processes. Whereas the methanolysis, for example, has a half-life of approximately 90 min. at 50°, the triethylamine-catalyzed reaction at 25° is complete in less than 1 min.

Discussion

The experimental results just described are singularly consistent and clear-cut, and may be summarized very simply: *in the presence of base, the solvolysis of alkanesulfonyl chlorides is accompanied by exchange of one and only one α hydrogen; in the absence of base no such exchange occurs.* If we designate the deuterated solvent as DZ (where Z may be OD, OCH$_3$, OCH(CH$_3$)$_2$, OC(CH$_3$)$_3$, NEt$_2$, or NHPh), then this may be symbolized

$$\text{RCH}_2\text{SO}_2\text{Cl} + \text{DZ} \xrightarrow{\text{base}} \text{RCHDSO}_2\text{Z} \qquad (1)$$

The significance of the term "base" in this context corresponds to that of common usage, thus pyridine and aniline are sufficiently basic to induce the exchange reaction (though apparently more slowly than the stronger bases[13]), whereas methanol and water are not.

*The Possibility of Mechanisms Not Involving Sulfenes.* It was pointed out in the introduction that the inter-

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(13) This is so with phenylmethanesulfonyl chloride, at least. In addition Truce, *et al.*, report[8] that no reaction occurs between methanesulfonyl chloride and pyridine under conditions in which the reaction with triethylamine is "immediate."

mediacy of a sulfene in these reactions would lead to the exchange of one hydrogen α to the sulfonyl group. This, of course, has been observed in the base-catalyzed reaction, and it follows that the observations are consistent with the sulfene mechanism. But the question immediately arises as to whether or not there are any mechanisms *not* involving sulfenes which can satisfactorily explain the observations described in this account.

It is obvious that any mechanism involving merely simple displacement at sulfur would not account for the formation of $PhCHDSO_2Z$ to the almost complete exclusion of $PhCH_2SO_2Z$ and $PhCD_2SO_2Z$. This point may be generalized to exclude any mechanism in which the reaction at C-1 is separate and distinct from that at the sulfur atom; in other words the two processes must be intimately associated. As another example, it is also possible to imagine a reaction when $Z = OD^-$, in which the deuteroxide anion attacks the sulfur forming a metastable anion in which the sulfur atom bears five substituents. From the fact that we find more than 90% of the monodeuterated product, it follows that in at least nine out of ten product-forming reactions, the metastable anion would have to lose an α proton *along with the chlorine*. In the simplest case this leads to the carbanion derived from the sulfonic acid ($R_2\bar{C}$-$SO_3D \leftrightarrow R_2C{=}\bar{S}O_3D$), and in our view is a process unlikely in the extreme.

These examples serve to illustrate that our experimental data in fact exclude a number of conceivable pathways for these reactions. Arguing more systematically, it is possible to analyze the over-all reaction into four logically separable steps: (1) loss of H, (2) gain of D, (3) loss of Cl, and (4) gain of Z. One can readily show that these four steps may be combined either consecutively or simultaneously to give 75 different sequences. Limiting the discussion to metathetical ionic reactions, as is evidently the case in these reactions, then one can show (by considerations similar to those in the previous paragraph) that all but *nine* of the 75 mechanistic sequences are highly improbable. The nine which are not excluded are those in which loss of H and Cl precedes the addition of either Z or D, *i.e., the mechanisms that are not excluded are all sulfene mechanisms*. In addition there are reasons for believing that the nine mechanisms may be limited further to the (three) sequences in which the first stage is a base-induced concerted elimination of HCl. The arguments for this last conclusion are suggestive rather than rigorous, and, like the reasons for excluding 66 of the 75 possible sequences, will not be taken up here because of limitations in space.

It should perhaps be mentioned at this point that there is very little direct evidence that the species obtained by abstracting HCl from, say, methanesulfonyl chloride has in fact the assumed sulfene structure (*i.e.*, I $\leftrightarrow$ II $\leftrightarrow$ III, etc.). What basis there is for this formulation stems from the nature of the products formed by its further reaction. These products would not be readily derivable from an alternative formulation such as IV, nor from the remotely conceivable methylene–sulfur dioxide "caged" pair (V). The relative significance of the canonical forms I, II, and III in sulfene cannot be assessed with certainty, though the reactions of sulfenes have led to the suggestion that II
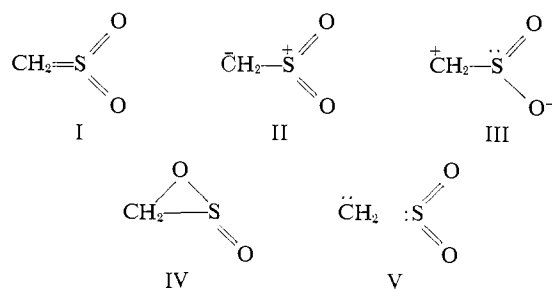
is more significant than III.[4b,14] In this context the recent determination by X-ray crystallography[15] of the structure of "thiourea dioxide" is perhaps significant. The bond lengths clearly establish structure VI and not the sulfene structure VII favored by Walter.[16] As "thiourea dioxide" differs markedly from sulfene in its chemical behavior, the formulations I $\leftrightarrow$ II for sulfene and VI for "thiourea dioxide" are therefore mutually consistent.

The Origin of Deviations from Strict Stoichiometry. The deuterium exchange reactions show certain deviations from the exact amount of hydrogen expected from eq. 1, there being in almost all cases a slight excess in the product of the isotope originally present in the sulfonyl chloride.

Assuming these discrepancies to be significant, they could be accounted for in various ways including the following: (i) a small but significant intervention of the direct displacement mechanism,[17] (ii) dilution of the solvent (or reagent) isotope with that from the portion of sulfonyl chloride which has already formed the sulfene, and (iii) a kinetic isotope effect in the addition step. There is evidence to show[18] that none of these effects taken singly could explain all of the observed deviations from eq. 1, and they must either be taken in combination or another effect invoked.

In view of the great speed of some of these reactions,[18] it is quite possible that the hydrogen abstracted from the sulfonyl chloride has not had sufficient time to diffuse very far from the sulfene before the sulfene is attacked. In that case the effective *local* concentration of the isotope originally on the sulfonyl chloride would be greater than that in the total medium. In our opinion this is a factor which well may account for much of the observed deviation from the stoichiometry of eq. 1, though unfortunately we cannot at present make a quantitative estimate of the extent of participation of this effect.

(14) G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957).

(15) R. A. L. Sullivan and A. Hargreaves, *Acta Cryst.*, **15**, 675 (1962).

(16) W. Walter, *Ann.*, **633**, 35 (1960).

(17) Perhaps the most likely example of this is the hydrolysis of methanesulfonyl chloride, the only reaction in which the deuteration corresponds to less than 90% of that expected for exchange of one hydrogen.

(18) For a more complete discussion of this and related points see T. Durst, Ph.D. Thesis, University of Western Ontario, 1964, pp. 34–38.

Conclusion

Since the inception of this study there have appeared a number of other reports on the chemistry of sulfenes which comprise a valuable complement to the deuteration studies, in the establishment of sulfenes as genuine intermediates in chemical transformations. Fusco and co-workers,[19] and independently Borowitz,[20] and Opitz and Fischer[21] have inquired into the nature of the reaction leading to four-membered ring sulfones from aliphatic sulfonyl halides, triethylamine, and activated olefins such as enamines and ketene acetals. By providing evidence which eliminates the most likely alternative mechanism, these studies give strong support to the view that these reactions are sulfene cycloadditions. Other recently reported reactions in which an aliphatic sulfonyl chloride is treated with triethylamine also very probably involve sulfenes.[6,22]

Many years ago Staudinger showed that sulfur dioxide reacts with diphenyldiazomethane to form tetraphenylethylene sulfone.[23] He suggested that sulfur dioxide and the diazo compound probably formed the sulfene which then reacted with more diazo compound. Support for this mechanism has recently been presented by Opitz and Fischer[21,24] who found that an aliphatic sulfonyl chloride with triethylamine in the presence of a diazo compound gives the corresponding ethylene sulfone. The formation of an ethylene sulfone does not always require the presence of a diazo compound: we have found[25] that cis-diphenylethylene sulfone (plus trans-stilbene) is formed by the reaction of phenylmethanesulfonyl chloride and triethylamine in certain inert solvents.

The above results are mentioned here primarily to demonstrate that there are a number of lines of evidence, quite separate from that which forms the substance of this paper, which point strongly to the existence of sulfenes as intermediates in certain reactions. In spite of the fact that no direct observation of a sulfene has yet, to our knowledge, been made, the sum of the indirect evidence leads to the conclusion, which for the reasons presented in this paper we believe to be inescapable, that sulfenes are indeed intermediates in certain chemical transformations.

Experimental Section[26]

Reaction of Phenylmethanesulfonyl Chloride with Triethylamine in the Presence of D_2O. Phenylmethane-

(19) R. Fusco, S. Rossi, and S. Maiorana, *Chim. Ind.* (Milan), **44**, 873 (1962).
(20) I. J. Borowitz, *J. Am. Chem. Soc.*, **86**, 1146 (1964).
(21) G. Opitz and K. Fischer, *Z. Naturforsch.*, **18b**, 775 (1963).
(22) (a) R. Fusco, S. Rossi, and S. Maiorana, *Chim. Ind.* (Milan), **45**, 564 (1963); (b) G. Opitz and E. Tempel, *Angew. Chem.*, **76**, 921 (1964).
(23) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).
(24) G. Opitz and K. Fischer, *Angew. Chem.*, **77**, 41 (1965).
(25) J. F. King and T. Durst, unpublished observations; *cf.* ref. 6b and 7.
(26) Infrared spectra were obtained using Beckman IR-5 and IR-7 spectrophotometers; unless otherwise stated all numerical values quoted for the infrared positions were obtained with the IR-7 instrument. The n.m.r. spectra were obtained using Varian A-60 and DP-60 instruments using tetramethylsilane as internal standard. The refractive indices were determined with a thermostatically controlled Bausch and Lomb refractometer. The melting points were determined on a Kofler hot stage and are uncorrected. Petroleum ether refers to the fraction of boiling range 35–60°. Phenylmethanesulfonyl chloride (sold as α-toluenesulfonyl chloride) and triethylamine were Eastman Kodak White Label grade and were used without further purification. The drying of organic extracts in reaction work-ups was carried out with sodium sulfate.

sulfonyl chloride (2.03 g.) was dissolved in dry dioxane (25 ml.) containing D_2O (4 ml.). Triethylamine (5 ml.) was added immediately and as quickly as possible. The reaction mixture was allowed to stand at room temperature for 1 min. then evaporated to dryness under reduced pressure. The residue was dissolved in water and washed with ether, and the aqueous phase was evaporated to dryness. The product was dissolved in chloroform (50 ml.), phosphorus pentachloride (4 g.) was added over a period of 15 min., and the reaction mixture then was washed with water. The chloroform layer was dried and the solvent was evaporated, yielding $PhCHDSO_2Cl$ (1.58 g., 77%), m.p. 91–92°, mixture melting point with the natural abundance isomer 91–92°. *Anal.* Calcd. for $PhCHDSO_2Cl$: 14.28 atom % excess D. Found: 13.92 atom % excess D. N.m.r. bands (CDCl₃) were found at 7.43 (singlet) and 4.82 p.p.m. (1:1:1 triplet, J = 2.1 c.p.s.); relative areas 5:1. Infrared peaks below 1500 cm.⁻¹ (0.5 M CHCl₃) were 1495 (m), 1455 (m), 1377 (vs), 1340 (w), 1230 (w), 1190 (w), 1184 (s), 1168 (s), 1152 (s), 1078 (w), 1030 (w), 1003 (w), 928 (w), 904 (w), 820 (m), 698 (s) cm.⁻¹.

Preparation of Phenylmethanesulfonyl-1,1-d_2 Chloride. Phenylmethanesulfonyl chloride (29 g.) was dissolved in dry dioxane (100 ml.) containing D_2O (20 g.). Triethylamine (50 ml.) was added in portions of 10 ml. during a period of 5 min. and the solution was allowed to stand for an additional 5 min. After the completion of the addition, the solvent was evaporated under reduced pressure and the crude product was dissolved in chloroform and treated with phosphorus pentachloride as in the previous experiment. The crude phenylmethanesulfonyl chloride which was obtained after washing with water and evaporating the chloroform, was treated as before. After a total of five such treatments phenylmethanesulfonyl-1,1-d_2 chloride (14.4 g.) was obtained, m.p. 90–92°, mixture melting point with the natural abundance compound 90–92°. The n.m.r. spectrum (CDCl₃) showed only aromatic protons at 7.45 p.p.m. (singlet). *Anal.* Calcd. for $C_7H_5D_2SO_2Cl$: 28.57 atom % excess D. Found: 27.70 atom % excess D. The infrared spectrum showed bands at 2258, 2240, 2165, 2145 cm.⁻¹ ascribable to C–D stretching. Other peaks in the infrared spectrum below 1500 cm.⁻¹ (0.5 M, CCl₄) were 1496 (m), 1453 (m), 1378 (vs), 1337 (w), 1235 (w), 1175 (vs), 1153 (sh), 1107 (w), 1080 (w), 1038 (w), 1027 (w), 1004 (w), 985 (w), 916 (w), 831 (w), 696 (vs) cm.⁻¹.

Reaction of Phenylmethanesulfonyl Chloride with Pyridine in the Presence of D_2O. Phenylmethanesulfonyl chloride (500 mg.) was dissolved in dry dioxane (20 ml.) containing D_2O (4 ml.). Dry pyridine (1 ml.) was added in one portion and the reaction mixture was allowed to stand for 1 min. at room temperature, then worked up in the same way as the analogous reaction with triethylamine. Silica gel chromatography of the product yielded, on elution with petroleum ether (b.p. 35–60°), phenylmethanesulfonyl-1-d chloride (357 mg., 71%), m.p. 91–92°, mixture melting point with the naturally abundant material 91–92°. The infrared and n.m.r. spectra were identical with those of the

Heavy water (99.7% D₂O) was supplied by Atomic Energy of Canada Ltd. The silica gel used was BDH suitable for chromatography.

phenylmethanesulfonyl-1-*d* chloride obtained by treating phenylmethanesulfonyl chloride with triethylamine in the presence of D₂O.

Reaction of Phenylmethanesulfonyl Chloride with Sodium Deuteroxide. Sodium deuteroxide solution (4 ml.), prepared by dissolving freshly cut sodium (0.5 g.) in D₂O (4 ml.), was added quickly to a solution of phenylmethanesulfonyl chloride (500 mg.) in dry dioxane (20 ml.). A precipitate formed immediately. The reaction was allowed to stand for 2 min., then made slightly acidic with 12 *N* HCl. The solvent was evaporated and the residue was suspended in chloroform and treated with phosphorus pentachloride. The product was washed with water and the chloroform was dried and evaporated. Chromatography on silica gel yielded on elution with 1:1 petroleum ether–benzene, phenylmethanesulfonyl-1-*d* chloride (287 mg., 57%), m.p. 91–92°, mixture melting point with the natural abundance sulfonyl chloride 90–92°. The infrared and n.m.r. spectra were identical with those of the phenylmethanesulfonyl-1-*d* chloride obtained by treating phenylmethanesulfonyl chloride with triethylamine in the presence of D₂O.

Isopropyl Phenylmethanesulfonate. Triethylamine (0.5 ml.) was added in one portion to a solution of phenylmethanesulfonyl chloride (300 mg.) dissolved in isopropyl alcohol (15 ml.). The reaction mixture was allowed to stand at room temperature for 1 min., poured into water, and extracted with ether. Evaporation of the ether gave the crude isopropyl ester (326 mg., 97%), which after recrystallization from methylene chloride–pentane melted at 46–47°. *Anal.* Calcd. for C₁₀H₁₄SO₃: C, 56.07; H, 6.59; S, 14.94. Found: C, 56.29; H, 6.53; S, 14.82. N.m.r. bands (CCl₄) were found at 1.25 (doublet, *J* = 6.2 c.p.s.), 4.32 (singlet), 4.75 (multiplet), and 7.41 p.p.m. (singlet); relative areas 6:2:1:5. Infrared peaks below 1500 cm.⁻¹ (0.6 *M*, CCl₄) were 1495 (w), 1465 (w), 1455 (w), 1410 (w), 1387 (m), 1365 (vs), 1345 (vs), 1268 (w), 1204 (m), 1173 (vs), 1158 (m), 1137 (m), 1095 (m), 1073 (w), 1030 (w), 920 (vs), 887 (vs), 825 (w), 696 (s) cm.⁻¹.

Reaction of Phenylmethanesulfonyl Chloride with Triethylamine in Isopropyl Alcohol-d. Isopropyl alcohol-*d* was prepared from aluminum isopropoxide according to Friedman and Turkevitch.²⁷ The deuterium content (92 ± 2% of active hydrogen) was estimated from the relative sizes of the O–H and O–D stretching bands in the infrared spectrum. Phenylmethanesulfonyl chloride (358 mg.) was dissolved in isopropyl alcohol-*d* (1 ml.) and allowed to react with triethylamine (0.5 ml.) for 1 min. The reaction mixture was worked up by pouring into water and extracting with ether. The yield of isopropyl ester was 135 mg. (35%), m.p. 46–47°, melting point on admixture with naturally abundant ester 46–47°. *Anal.* Calcd. for C₁₀H₁₃DSO₃: 7.14 atom % excess D. Found: 6.49 atom % excess D. N.m.r. bands (CCl₄) were found at 1.29 (doublet, *J* = 6.2 c.p.s.), 4.31 (broad "singlet"), 4.75 (multiplet), and 7.38 p.p.m. (singlet); relative areas 6:1:1:5. Infrared peaks below 1500 cm.⁻¹ (0.6 *M*, CCl₄) were 1496 (w), 1465 (w), 1455 (m), 1388 (m), 1365 (vs), 1345 (vs), 1286 (w), 1270 (w), 1232 (w), 1223 (w), 1196 (m), 1188 (vs),

1175 (vs), 1155 (s), 1095 (s), 1077 (w), 1031 (w), 940 (s), 920 (vs), 887 (s), 830 (w), 825 (w), 695 (s) cm.⁻¹.

Deuterium Exchange in Isopropyl Phenylmethanesulfonate. Isopropyl phenylmethanesulfonate (175 mg.) was dissolved in isopropyl alcohol-*d* (2 ml.). Triethylamine (0.4 ml.) was added in one portion and the solution was heated in an oil bath at 50 ± 1° for 1 hr. The reaction mixture was poured into water and extracted with ether. Evaporation of the ether yielded isopropyl phenylmethanesulfonate (145 mg.), m.p. 46–47°. Found: 1.04 atom % excess D, equivalent to the incorporation of an average of 0.146 atom of deuterium per molecule.

Methyl Phenylmethanesulfonate. Triethylamine (1 ml.) was added in one portion to a solution of phenylmethanesulfonyl chloride (400 mg.) in methanol (20 ml.). The methanol was evaporated after 5 min. and the residue was extracted with ether and washed with 1 *N* HCl. The ether layer was dried and evaporated giving methyl phenylmethanesulfonate (376 mg., 96%), m.p. 61–62° (lit.²⁸ m.p. 61–62°). N.m.r. bands (CDCl₃) were found at 7.38 (singlet), 4.22 (singlet), and 3.64 p.p.m. (singlet); relative areas 5:2:3. Infrared peaks below 1500 cm.⁻¹ (0.5 *M*, CHCl₃) were 1495 (m), 1456 (s), 1409 (w), 1365 (vs), 1270 (w), 1171 (vs), 1160 (sh), 1138 (s), 1075 (w), 1030 (w), 998 (vs), 920 (w), 882 (s), 825 (sh), 815 (vs), 700 (vs) cm.⁻¹.

Reaction of Phenylmethanesulfonyl Chloride with Triethylamine in Methanol-d. Phenylmethanesulfonyl chloride (160 mg.) was dissolved in methanol-*d* (0.8 ml.), prepared from sodium methoxide according to Hill, *et al.*²⁹ (estimated deuterium content 95 ± 2% of active hydrogen), and was allowed to react with triethylamine (0.2 ml.) for 1 min. The reaction was worked up by pouring into water and extracting with ether. The yield of ester was 39 mg. (25%), m.p. 61–62°, mixture melting point with natural abundance methyl phenylmethanesulfonate 61–62°. The infrared spectrum of the product was identical with that obtained when PhCD₂SO₂Cl was treated with triethylamine in the presence of methanol (see below). In a separate experiment phenylmethanesulfonyl chloride (191 mg.) and methanol-*d* (35 mg.) were dissolved in anhydrous ether (4 ml.), and the solution immediately was treated with triethylamine (0.3 ml.). The infrared spectrum of the product was almost identical with that obtained above and showed no trace of *trans*-stilbene. What differences there were could be attributed to a slightly greater amount of the natural abundance ester present in the sample. Finally, phenylmethanesulfonyl chloride (85 mg.) and methanol-*d* (35 mg.) were dissolved in dry cyclohexane (10 ml.) and treated with triethylamine (0.3 ml.) as above. The infrared spectrum of the product was almost identical with that of PhCHDSO₃Me and showed no trace of oxythiobenzoyl chloride. The small differences in spectra were again traceable to the presence of a greater amount of naturally abundant ester.

Reaction of Phenylmethanesulfonyl-1,1-d₂ Chloride with Triethylamine in Methanol. Phenylmethanesulfonyl-1,1-*d₂* chloride (300 mg.) was dissolved in meth-

(27) L. Friedman and J. Turkevitch, *J. Am. Chem. Soc.,* 74, 1666 (1952).

(28) C. K. Ingold, E. H. Ingold, and F. R. Shaw, *J. Chem. Soc.,* 813 (1927).

(29) D. G. Hill, B. Stewart, S. W. Kantor, W. A. Judge, and C. R. Hauser, *J. Am. Chem. Soc.,* 76, 5129 (1954).

anol (10 ml.). Triethylamine (0.5 ml.) was added in one portion and the reaction mixture allowed to stand at room temperature for 5 min. The methanol was evaporated and the residue extracted with ether. Evaporation of the ether gave $PhCHDSO_3CH_3$ (281 mg., 96%), m.p. 61–62°, mixture melting point with the natural abundance ester 61–62°. N.m.r. bands ($CDCl_3$) appeared at 7.35 (singlet), 4.21 (partially resolved triplet, $J \sim 2$ c.p.s.), and 3.67 p.p.m. (singlet); relative areas 5:1:3. Infrared peaks below 1500 cm.$^{-1}$ (0.5 M, $CHCl_3$) were 1495 (m), 1454 (s), 1363 (vs), 1285 (w), 1268 (w), 1234 (m), 1186 (vs), 1167 (vs), 1148 (vs), 1051 (w), 1027 (w), 998 (vs), 938 (w), 908 (w), 835 (m), 813 (s), 698 (vs) cm.$^{-1}$. *Anal.* Calcd. for $C_8H_9DSO_3$: 10.00 atom % excess D. Found: 9.72 atom % excess D.

Attempted Preparation of t-Butyl Phenylmethanesulfonate. Phenylmethanesulfonyl chloride (1.0 g.) and *t*-butyl alcohol (3 ml.) were dissolved in methylene chloride (30 ml.). The solution was cooled to −60° and triethylamine (1.5 ml.) was added over a period of about 2 min. After an additional 2 min., the reaction was washed with water and methylene chloride. The methylene chloride solution was dried and the solvent was evaporated without warming yielding a colorless oil (712 mg.). When the oil was allowed to warm up to room temperature, bubbles formed in it. An infrared spectrum taken after 10 min. showed only phenyl-methanesulfonic acid.

In another experiment phenylmethanesulfonyl chloride (100 mg.) was dissolved in *t*-butyl alcohol (5 ml.), and the solution was treated with triethylamine (0.1 ml.). The reaction mixture was allowed to stand at room temperature for 5 min., then extracted with water and ether. Evaporation of the ether layer yielded a colorless oil (32 mg.) whose infrared spectrum (CCl_4, IR-5) showed strong peaks at 1377, 1165, and 922 cm.$^{-1}$.

Reaction of Phenylmethanesulfonyl Chloride with Tri-ethylamine in t-Butyl Alcohol-d. Phenylmethanesulfonyl chloride (191 mg.) was dissolved in *t*-butyl alcohol-*d* (2 ml.), prepared from sublimed potassium *t*-butoxide and D_2O (estimated deuterium content 90 ± 3% of the active hydrogen). Triethylamine (0.3 ml.) was added in one portion and the reaction mixture was allowed to stand at room temperature for about 10 min., then washed with water and ether. The aqueous phase was taken down to dryness and the residue was treated with phosphorus pentachloride in the usual manner. The yield of deuterated phenylmethanesul-fonyl chloride was 131 mg. (68%). The infrared spectrum was almost identical with that of the phenylmeth-anesulfonyl-1-*d* chloride obtained by treating phenyl-methanesulfonyl chloride with triethylamine in the presence of D_2O. The small differences were assign-able to the presence of some naturally abundant material in the sample. The n.m.r. spectrum ($CDCl_3$) showed peaks at 7.43 and 4.82 p.p.m.; relative areas 5.0:1.2.

Reaction of Phenylmethanesulfonyl-1,1,-d₂ Chloride with Diethylamine. Diethylamine (Fisher reagent grade, 2 ml.) was added as quickly as possible to meth-ylene chloride (20 ml.) containing phenylmethane-sulfonyl-1,1-d_2 chloride (625 mg.). After 1 min., the reaction was worked up by washing with water, drying,

and evaporating the methylene chloride. Recrystalliza-tion from ether–pentane gave white plates, m.p. 32–33°, mixture melting point with the naturally abundant amide[28] 32–33°. *Anal.* Calcd. for $C_{11}H_{16}DNO_2S$: 5.88 atom % excess D. Found: 6.12 atom % excess D. The n.m.r. spectrum (CCl_4) showed bands at 1.08 (triplet), 3.09 (quartet), 4.19 (broadened peak), and 7.37 p.p.m. (singlet); relative areas 3:2:1:5.

Reaction of Phenylmethanesulfonyl-1,1-d₂ Chloride with Aniline. A solution of phenylmethanesulfon-yl-1,1-d_2 chloride (302 mg.) and aniline (1.0 ml.) in benzene (25 ml.) was refluxed for 2 hr. and then washed with 2 *N* HCl and dried, and the solvent was evapo-rated. The yield of the phenylmethanesulfonanilide was 302 mg. (78%), m.p. 102–103°, mixture melting point with a sample of the natural abundance anilide[30] 101–103°. *Anal.* Calcd. for $C_{13}H_{12}DNSO_2$: 7.69 atom % excess D. Found: 8.13, 8.20 atom % excess D. N.m.r. bands were at 4.3 (broadened band) and 7.2 to 7.4 p.p.m. (complex multiplet); relative areas 1:10.

Reaction of Methanesulfonyl Chloride with D₂O. Methanesulfonyl chloride (Fisher reagent grade, 4.40 g.) was dissolved in dry dioxane (25 ml.) containing D_2O (18 ml.). The solution was cooled to −5°, and tri-ethylamine (5 ml.) was added over a period of 5 min. The reaction was left at room temperature for an addi-tional 5 min. The solvent was then evaporated under reduced pressure, and the residue was dissolved in water and washed with ether. The aqueous phase was taken down to dryness. The residue was dissolved in chloro-form (50 ml.) and phosphorus pentachloride (8 g.) was added in small portions over a period of about 15 min. The reaction mixture was washed with water, the chloroform solution was dried, and the solvent was evaporated yielding the methanesulfonyl chloride (3.20 g., 73%), b.p. 58–61° (15 mm.), $n^{25}D$ 1.4489. Johnson and Sprague[31] report $n^{25}D$ 1.4490 for the natural abundance material. *Anal.* Calcd. for CH_2DSO_2Cl: 33.32 atom % excess D. Found: 24.00 atom % excess D. The n.m.r. spectrum (CCl_4) showed a triplet at 3.63 ($J = 2.0$ c.p.s.) superimposed on a singlet at 3.65 p.p.m.

Deuterated methanesulfonyl chloride (350 mg.) from above was dissolved in benzene (15 ml.) containing *p*-toluidine (700 mg.). The reaction mixture was warmed on a steam bath for 1 hr. The solution was cooled and washed with 2 *N* HCl. The benzene layer was dried and evaporated yielding the methanesulfontoluidide (175 mg., 29%), m.p. 101–102°, mixture melt with an authentic sample[32] of the natural abundance amide, 101–103°. The n.m.r. spectrum ($CDCl_3$) of the deu-terated material showed bands at 2.33, 2.99, and 7.22 p.p.m. (all singlets). Integration of the 2.33- and 2.99-p.p.m. peaks gave a ratio of 2.20:3, the calculated ratio on the basis of $CH_2DSO_2NHC_6H_4CH_3$ is 2:3. The value found corresponds to a minimum deuterium content of 0.8 atom per molecule.

The anilide of the deuterated methanesulfonyl chlo-ride was prepared in the same way. Recrystallization from chloroform–pentane gave white needles, m.p.

(30) E. Fromm and J. de Seixas Palma, *Ber.*, **39**, 3308 (1906).
(31) T. B. Johnson and J. M. Sprague, *J. Am. Chem. Soc.*, **58**, 1348 (1936).
(32) C. D. Marvel, M. D. Helfrick, and J. P. Belsley, *ibid.*, **51**, 1272 (1929).

98–99°; mixture melting point with an authentic sample[32] of the natural abundance compound 97–99°.

Reaction of Ethanesulfonyl Chloride with D_2O. Ethanesulfonyl chloride (4.52 g.) was dissolved in dry dioxane (25 ml.) containing D_2O (18 ml.). Triethylamine (50 ml.) was added over a period of 5 min. and the solution was allowed to stand for an additional 5 min., then worked up as in the case of methanesulfonyl chloride yielding monodeuterated ethanesulfonyl chloride (3.17 g., 71%) b.p. 65–66° (15 mm.), $n^{25}D$ 1.4506. Johnson and Sprague[31] report $n^{25}D$ 1.4506 for the natural abundance isomer. *Anal.* Calcd. for $C_2H_4DSO_2Cl$: 20.00 atom % excess D. Found: 18.55 atom % excess D. The n.m.r. spectrum (CCl_4) showed a doublet ($J = 7.2$ c.p.s.) of triplets ($J = 1.1$ c.p.s.) at 1.62 and a quartet ($J = 7.2$ c.p.s.) of triplets ($J = 2.2$ c.p.s.) at 3.65 p.p.m. The relative areas were 3:1.1.

The aniline and *p*-toluidine derivatives of the deuterated ethanesulfonyl chloride were prepared in the same way as those of the methanesulfonyl chloride; anilide m.p.[33] (i) from $CH_3CH_2SO_2Cl$, 57–58°; (ii) from CH_3CHDSO_2Cl, 56–58°; m.m.p. (i) and (ii), 56–58°; toluidides m.p.[34] (i) from $CH_3CH_2SO_2Cl$, 76–78°; (ii) from CH_3CHDSO_2Cl, 77–78°; m.m.p. (i) and (ii), 76–78°.

Reaction of 2-Phenylethanesulfonyl Chloride with D_2O. 2-Phenylethanesulfonyl chloride[35] (410 mg.) was dissolved in dioxane (20 ml.) containing D_2O (5 ml.). Triethylamine (2.0 ml.) was added as quickly as possible. The reaction was allowed to stand at room temperature for 10 min. and then worked up as in the solvolysis of phenylmethanesulfonyl chloride. Silica gel chromatography of the product obtained from the phosphorus pentachloride reaction, gave an oil (315 mg.) on elution with 1:1 petroleum ether–benzene. Recrystallization from petroleum ether gave long white

(33) W. Autenrieth and P. Rudolph, *Ber.*, **34**, 3467 (1901).

(34) N. N. Mel'nikov, E. M. Sokolova, and P. P. Trunov, *Zh. Obshch. Khim.*, **29**, 529 (1959).

(35) E. B. Evans, E. E. Mabbot, and E. E. Turner, *J. Chem. Soc.*, 1159 (1927).

needles, m.p. 31–33°, mixture melting point with a sample of natural abundance 2-phenylethanesulfonyl chloride 31–33°. The n.m.r. spectrum showed aromatic protons at 7.20 (singlet) and aliphatic protons at 3.95 to 3.10 p.p.m. (complex multiplet) in the ratio of 5:3. *Anal.* Calcd. for $C_8H_8DSO_2Cl$: 11.11 atom % excess D. Found: 10.45 atom % excess D.

Hydrolysis of Phenylmethanesulfonyl-1,1-d_2 Chloride without Added Base. Phenylmethanesulfonyl-1,1-d_2 chloride (400 mg.) was dissolved in dioxane (12 ml.) and water (12 ml.) and the solution was warmed at 50° for 90 min. The reaction mixture was extracted with ether; the product (97 mg., 24%) obtained on evaporation of the ether was identified as phenylmethanesulfonyl-1,1-d_2 chloride by its infrared spectrum. The aqueous layer was taken down to dryness. Treatment of the residue with phosphorus pentachloride in the usual manner gave $PhCD_2SO_2Cl$ (211 mg., 53%), m.p. 90–92°. The infrared spectrum was identical with that of an authentic sample.

Methanolysis of Phenylmethanesulfonyl-1,1-d_2 Chloride without Added Base. Phenylmethanesulfonyl-1,1-d_2 chloride (690 mg.) was dissolved in methanol (Fisher Spectranalyzed, 25 ml.) and warmed in an oil bath at 50° for 90 min. The methanol was evaporated and the product was chromatographed on silica gel (30 g.). Elution with 1:1 petroleum ether–benzene gave phenylmethanesulfonyl-1,1-d_2 chloride (304 mg., 49%) whose infrared spectrum was identical with that of the starting material. Elution with 9:1 benzene–ether yielded methyl phenylmethanesulfonate-1,1-d_2 (236 mg., 35%), m.p. 61–62°, mixture melting point with the natural abundance ester 61–62°. *Anal.* Calcd. for $C_8H_8D_2SO_3$: 20.00 atom % excess D. Found: 19.50 atom % excess D. N.m.r. bands ($CDCl_3$) were found at 7.38 (singlet) and 3.73 p.p.m. (singlet). Infrared peaks below 1500 cm.$^{-1}$ (0.5 M, $CHCl_3$) were 1495 (m), 1451 (s), 1360 (vs), 1282 (m), 1180 (vs), 1150 (sh), 1053 (w), 1038 (w), 1028 (m), 1012 (vs), 993 (vs), 915 (w), 850 (s), 806 (s), 700 (s) cm.$^{-1}$. C–D stretching bands were at 2240 (vw) and 2156 (vw) cm.$^{-1}$.

Iminolactones. I. The Mechanism of Hydrolysis

Gaston L. Schmir and Bruce A. Cunningham[1]

Contribution from the Department of Biochemistry, Yale University, New Haven, Connecticut 06510. Received August 18, 1965

The hydrolysis of the iminolactone 2-phenyliminotetrahydrofuran (III) has been investigated in the pH range 0–14 at 30°. The rate–pH profile resembles those reported for the hydrolyses of thiazolines, oxazolines, and Schiff bases. The nature of the hydrolysis products, however, varies with pH. There occurs a gradual transition from the formation of aniline (and butyrolactone) at acid pH to the appearance of γ-hydroxybutyranilide in basic solution; at about pH 7.1, equal amounts of the two products are formed. These findings have necessitated an alteration of the accepted mechanism of imine hydrolysis; it is suggested that, depending upon pH, the hydrolysis of III proceeds either through a neutral carbinolamine intermediate or through its conjugate base, the choice of pathway dictating the identity of the product.