

precipitate was treated with 50 ml. of 5% sodium hydroxide solution (or 5% bicarbonate solution) to take up the acids. In either case the aqueous alkaline solution was added dropwise with stirring to a mixture of 50 ml. of concentrated hydrochloric acid and 100 g. of ice. The precipitate was collected by filtration, crystallized from alcohol-water, and dried. The percentage yields given in the tables as well as the melting points refer to this product. Where a sample for analysis was desired, the product was recrystallized, usually from alcohol-water, and finally dried *in vacuo*.

In some cases a measure of unreacted aldehyde was found by examining the ethereal solution from which acids had been removed with aqueous alkali. When benzaldehyde was used, unreacted aldehyde was oxidized with alkaline permanganate and the benzoic acid collected and weighed. In other cases the aldehyde was recovered as the 2,4-dinitrophenylhydrazone.

Ozonolysis of α -Allyl-2-methoxycinnamic Acid.—Ozonized oxygen was bubbled into a solution of 0.436 g. (2.00

millimoles) of α -allyl-2-methoxycinnamic acid in 30 ml. of ethyl acetate at -80° . When 2.00 millimoles of ozone had been absorbed (after 4–5 minutes) the reaction was interrupted, and the ethyl acetate removed by evaporation in a stream of nitrogen. Zinc dust (0.65 g.) and ice-water (50 ml.) was added to the residual oil, and the mixture was stirred for 30 minutes. More water (200 ml.) was added and the mixture was distilled directly into a solution of 0.56 g. (4 millimoles) of dimethyldihydroresorcinol in 200 ml. of water. After 3 days in the refrigerator, the separated solids were collected and air-dried. The derivative (0.28 g., m.p. $158-170^\circ$) after three crystallizations from alcohol-water weighed 0.08 g. (14%) and melted at $185-186.5^\circ$. The mixture melting point with the same derivative of formaldehyde (m.p. $187.5-188.5^\circ$) was $186-187^\circ$.

When allylmalonic acid was ozonized in a similar manner, formaldehyde as its dimethyldihydroresorcinol derivative was obtained in 34% yield.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Ionic Fission of the O–O Bond in *t*-Butyl Arylpersulfonates¹

BY PAUL D. BARTLETT AND BAYARD T. STOREY

RECEIVED MAY 3, 1958

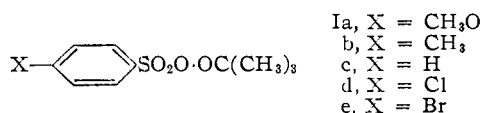
t-Butyl benzenepersulfonate, a new class of perester, and four *p*-substitution products have been prepared. These decompose quantitatively in methanol to give acetone and arylsulfonic acid by ionic cleavage of the peroxide bond. Kinetic studies of the decomposition of *t*-butyl pertosylate in methanol and aqueous methanol have been carried out. The reaction is subject to unusual salt effects which show pronounced maxima with salt concentration and which disappear almost completely with the addition of water to the methanol. In contrast to 9-decalyl perbenzoate, *t*-butyl pertosylate shows strong negative deviation from the Grunwald–Winstein equation near the methanol end of a series of methanol–water mixtures, but obeys this equation over the rest of the range. A mechanistic interpretation of this behavior is offered.

Introduction

Peresters derived from *t*-butyl hydroperoxide usually decompose by cleavage to radicals. One exception discovered recently^{2a,b} is *t*-butyl trifluoroperacetate, which seems to decompose in part by ionic cleavage. This suggested that a *t*-butyl perester derived from a sufficiently strong acid might well undergo ionization of the oxygen–oxygen bond to the exclusion of homolytic cleavage. The strongest organic acids available are the sulfonic acids and so the possibility of preparing *t*-butyl persulfonates was investigated.

Products of Decomposition

Five *t*-butyl arylpersulfonates were prepared: the *p*-methoxybenzene, *p*-toluene, benzene, *p*-chlorobenzene and *p*-bromobenzene peresters, Ia–e.



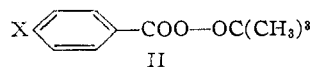
The first two are relatively stable, decomposing exothermically (and usually quite violently) at room temperature after about 5–10 minutes. The benzenepersulfonate is of intermediate stability, and the *p*-chloro and *p*-bromo compounds are quite unstable and hard to handle. (All may be left from two to four weeks in the freezer.) The *p*-nitro compound could not be prepared. The order of stability indicates that decomposition of these

peresters is favored by anionic stability of the sulfonate group.

Determination of the products of decomposition of the peresters in methanol at room temperature confirms the ionic mechanism in this solvent. Only two products are isolated and these in quantitative yield: acetone and the appropriate arylsulfonic acid. Acetone was determined gravimetrically as the 2,4-dinitrophenylhydrazone. Yields ranged from 95 to 99% and the purity of the unrecrystallized material gave no suggestion of side products. The sulfonic acid was determined both by titration and by isolating and weighing the sodium salt. Yields were consistently $100 \pm 1\%$. *t*-Butyl pertosylate gave the same result in aqueous methanol (mole fraction of water 0.1 and 0.2.). As a control, *t*-butyl hydroperoxide was decomposed at 100° in methanol, conditions which should give *t*-butoxy radicals. Formaldehyde was isolated as the 2,4-dinitrophenylhydrazone in 65–70% yield, presumably from attack by *t*-butoxy radicals on the solvent. No formaldehyde was present in the products of the persulfonate decompositions.

Kinetic Evidence

In the radical-producing thermal decomposition



of *t*-butyl perbenzoates II,³ the Hammett equation⁴ is obeyed, a plot of $\log k$ against σ having a slope

(3) A. T. Blomquist and I. A. Berstein, *THIS JOURNAL*, **73**, 5546 (1951).

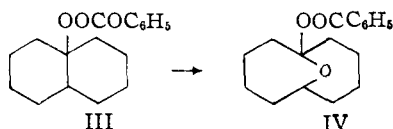
(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

(1) This paper was presented at the Spring Meeting of the National Academy of Sciences, Washington, D. C., April 29, 1958.

(2) (a) P. D. Bartlett and R. R. Hiatt, *THIS JOURNAL*, **80**, 1398 (1958); (b) P. D. Bartlett, *Experientia*, Suppl. VII, 275 (1957).

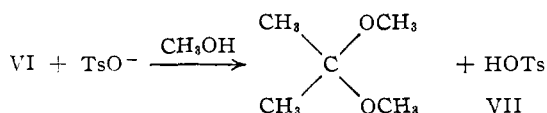
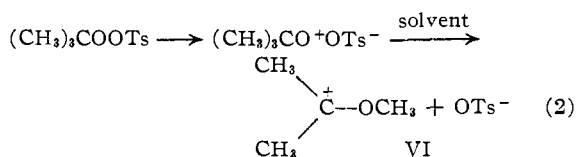
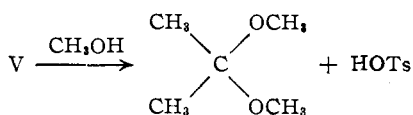
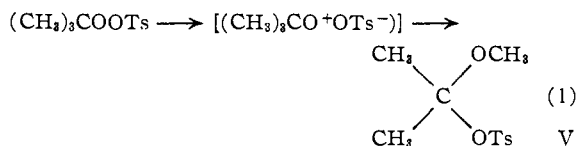
(ρ) of -0.9 at 100° . A similar plot (Fig. 1) for the *t*-butyl persulfonates I is also linear, but has a positive value of ρ , $+1.36$, the direction of the effect being appropriate to a process in which the substituted portion of the reactant molecule becomes an anion.

With esters of tertiary hydroperoxides other than *t*-butyl, ionic rearrangements are well known, a now familiar example being 9-decalyl perbenzoate (III).⁵ This ester, while responding to ionizing media, has been shown to rearrange directly to an acylal (IV) without the formation of free ions in



the process^{6,7} and without the oxygen atoms of the benzoate group becoming equivalent.⁸ For *p*-substituted 9-decalyl perbenzoates, Hammett's ρ is also positive, $+1.34$, compared to $+1.36$ for the persulfonates.

In the case of *t*-butyl pertosylate, the acetone and sulfonic acid observed might result from a similar completed rearrangement followed by hydrolysis of the hemiketal sulfonate V, or from attack of solvent upon a cation (VI) representing a more complete ionization than occurs in the case of 9-decalyl perbenzoate.



A rough estimate of the rate of solvolysis of the acetone hemiketal tosylate resulting from rearrangement can be made, starting from the data of Salomaa⁹ on the rate of solvolysis of chloromethyl methyl ether in methanol-dioxane mixtures. Extrapolation of the rate constants to pure methanol gives $k = 0.26 \text{ sec}^{-1}$ at 5° and $k = 2.2 \text{ sec}^{-1}$ at 25° . Salomaa's data show that these ethers solvolyze by ionization

- (5) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).
 (6) P. D. Bartlett and J. L. Kice, *THIS JOURNAL*, **75**, 5591 (1953).
 (7) H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).
 (8) D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957).
 (9) P. Salomaa, *Ann. Acad. Turkuensis*, **A14** (1953).

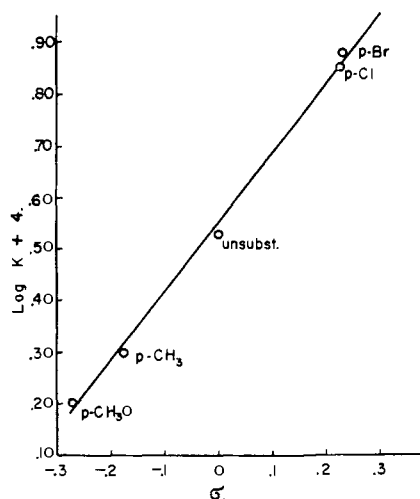
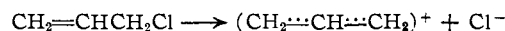


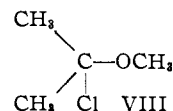
Fig. 1.—Reaction rate constants of *p*-substituted *t*-butylperoxy benzenesulfonates in methanol at 4.50° , plotted according to the Hammett equation.



Ionization of allylic chlorides is analogous to that of the ethers



Allyl chloride and α,α -dimethylallyl chloride in 50% ethanol at 25° (assumed to be good ionizing conditions) have rate constants for solvolysis¹⁰ in the ratio $1:1.3 \times 10^6$. Applying this factor to the haloethers, the rate constants for α -chloroisopropyl methyl ether (VIII) are $0.34 \times 10^6 \text{ sec}^{-1}$



at 5° and $2.9 \times 10^6 \text{ sec}^{-1}$ at 25° . The increase in rate on changing from chloride to tosylate may be estimated from the solvolysis rates of isopropyl chloride and tosylate in 80% ethanol at 50° (the best ionizing conditions for which data are available).¹¹ The tosylate reacts 3500 times as fast as the chloride. This gives 10^9 sec^{-1} at 5° and 10^{10} at 25° as the estimated solvolysis rate constants for the hemiketal tosylate. These numbers, corresponding to half-lives of less than 10^{-9} second, mean effectively that the α -methoxyisopropyl cation VI, once formed from *t*-butyl pertosylate, will never be found combined with the tosylate anion as V, but as products of solvent attack—the ketal VI or the related hemiketal, both of which will yield acetone 2,4-dinitrophenylhydrazones in acid solution as easily as acetone itself.

t-Butyl pertosylate decomposes in benzene and chlorobenzene to give dark red solutions of acidic tars. The same is true in styrene, and the styrene is not polymerized by the perester. If the colored products resulted from cleavage of the perester to radicals, styrene should act as an interceptor and should itself be polymerized. Addition of a small amount of pyridine to the styrene does eliminate the

- (10) R. H. De Wolfe and W. G. Young, *Chem. Revs.*, **56**, 786 (1956), Table 6.
 (11) A. Streitwieser, *ibid.*, **56**, 654 (1956), Table 36.

tar formation and gives a precipitate of pyridinium tosylate. This is evidence that the perester undergoes ionic decomposition even in non-polar solvents. The colored material may arise from the action of *p*-toluenesulfonic acid on isopropenyl methyl ether formed during the decomposition.

The kinetics of the decomposition of *t*-butyl pertosylate was investigated by iodometric titration over a range of solvents from anhydrous methanol to methanol containing 8 *M* water. The non-linear variation of rate constant in these media is shown in Fig. 2. In view of the almost

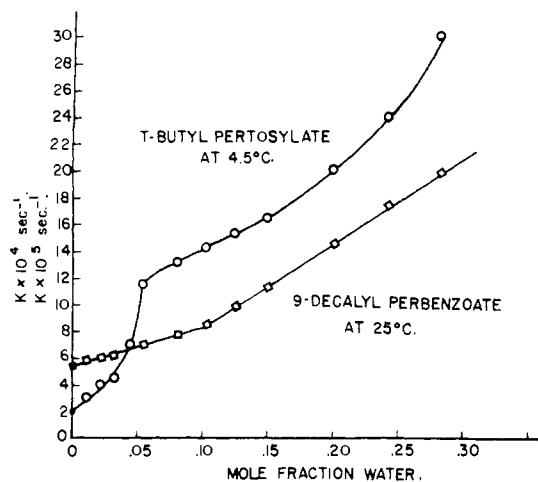


Fig. 2.—Reaction rate constants of peresters in methanol-water mixtures: circles, *t*-butyl pertosylate at 4.5°, $k \times 10^4$; squares, 9-decalyl perbenzoate at 25°, $k \times 10^5$.

certainly ionic nature of the reaction it was desirable to compare the effect of medium upon it with that of the same range of media on the ionization rate of *t*-butyl chloride, *i. e.*, to apply the equation of Grunwald and Winstein¹²

$$\log(k/k_0) = mY$$

If the pronounced irregularity in the plot of Fig. 2 were to give way to any greater linearity in a plot of $\log k$ against *Y*, it would be necessary that the values of *Y* in the region in question should deviate from the empirical equation given by Fainberg and Winstein.¹³ Since this equation was based on solutions rather far apart in composition for our purpose, we have measured the rate of solvolysis of *t*-butyl chloride in the same series of aqueous methanol solvents used for the studies of *t*-butyl pertosylate, and have thus determined the *Y* values of these solvents directly.

The plot of $\log k$ for *t*-butyl pertosylate at 4.5° against the corresponding *Y* values, shown in Fig. 3, indeed shows a regularity. As the water content of the medium is decreased, a straight Grunwald-Winstein plot is obtained down to 1.4 *M* water, its slope yielding an *m* value of 0.44; below this point $\log k$ drops sharply with a new slope of 5.1, and in pure methanol the rate is about one-fifth of the value indicated by the extrapolated line.

For comparison the related ionic rearrangement

(12) E. Grunwald and S. Winstein, *THIS JOURNAL*, **70**, 846 (1948).

(13) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

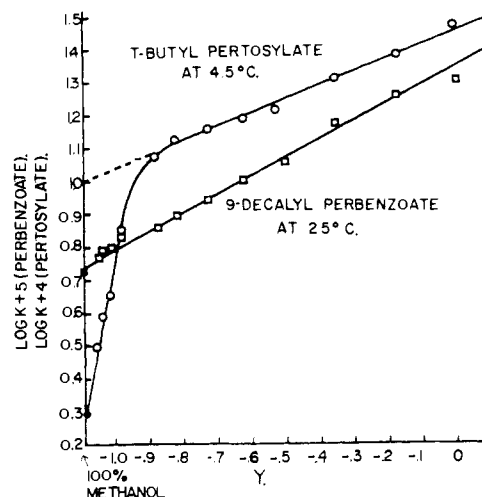


Fig. 3.—Effect of solvent composition (methanol-water mixtures) upon rate constant for reaction of *t*-butyl pertosylate at 4.5° (circles) and of 9-decalyl perbenzoate at 25° (squares) plotted according to the Grunwald-Winstein equation, $\log(k/k_0) = mY$. The abscissas are *Y* values based on the solvolysis rates of *t*-butyl chloride in the same solvent mixtures.

of 9-decalyl perbenzoate was studied kinetically at 25° in the same series of solvents, with results which are also shown in Figs. 2 and 3. Here, despite a little roughness of the fit in the low-water region, the relationship between $\log k$ and *Y* is linear, with no such trend as in the case of the pertosylate. From the slopes we find an *m* value of 0.57 for the perbenzoate compared to 0.44 for the pertosylate. These reactions are therefore approximately half as sensitive to changes in the ionizing power of a solvent medium as is the ionization of *t*-butyl chloride. This procedure now constitutes a quantitative way of applying the Meerwein-Criegee criterion of an ionic mechanism, namely, the comparison of reaction rates in media of different ionizing power.

The measurements for *t*-butyl pertosylate were made at both 4.50° and -5.87°, resulting in the activation parameters

	ΔH^\ddagger , kcal.	ΔS^\ddagger , cal./degree
Observed rate in methanol	18.9	-6.9
Extrapol. from Grunwald-Winstein plot	21.7	+5.8

Interpretation of Results

The Grunwald-Winstein equation has been applied to a number of reactions of solvolytic type whose rates are controlled by the ionization of an organic chloride, carboxylic or sulfonic ester. The ionic fission of an O—O bond can be governed by the same factors in a solvent as that of a C—O or C—Cl bond. This is shown by the fact that the rearrangement of 9-decalyl perbenzoate is linearly correlated with the solvolysis of *t*-butyl chloride over the same range of solvent composition now under investigation for *t*-butyl pertosylate. If we accept this view, the behavior of *t*-butyl pertosylate in methanol containing less than 2% water presents a most unusual and interesting problem. We must

suppose that the extrapolation of the log k - Y plot from the more aqueous media represents the rate of some true ionization process all the way down to pure methanol. However, for some reason this ionization process has ceased to be in complete control of the observed reaction, namely, the loss of peroxidic reactivity, in the solvent mixtures low in water. The work of Winstein and his co-workers has provided evidence of several distinguishable intermediates in the course of a solvolysis, and we may examine these for their possible bearing on the mechanism of an ionic O-O fission.¹⁴

First there is the ion pair W-II,¹⁵ which is characterized by immunity to direct attack by ions and other nucleophiles, and by a bond which, in changing from covalent to ionic, has not become stretched to the extent of admitting a solvent molecule between its member atoms. This species W-II is characterized by a symmetry which enables it to revert to an isomer of the starting material ("internal return") when its cationic member is allylic, homoallylic or formed with anchimeric assistance of a neighboring group. The extent of this reversion is influenced by the structure of the solvolysing compound and by the solvent, but not by changing concentration of any outside reagent molecule. Should semantic fashion eventually disqualify the term, "ion pair," for this species, these operational criteria would remain to define it. (It may be noted, however, that none of these properties of W-II establishes it firmly as a molecular species resting at an energy minimum.)

The species W-II, by more complete solvation, is changed to an ion pair W-III, identical with the "ion pair" of classical solution theory, which is held together exclusively by electrostatic forces but which contributes nothing to the conductivity of the solution. The outstanding chemical characteristic of species W-III is its extreme reactivity toward ionic reagents whose component ions, like the perchlorate ion, have no particular nucleophilic or electrophilic character.¹⁴ The pair W-III returns easily to the starting material, but is diverted from such return by any reagent which will bring about ionic realignment, and this includes neutral salts functioning at concentrations of less than 0.02 M (the "special salt effect" of Winstein and co-workers). In those cases where return from an ion pair equilibrates d - and l -isomers it has been possible to measure independently the amounts of return from W-II and W-III; it is found that the relative importance of the two is strongly influenced by solvent, as would be expected since it is further solvation which converts W-II into W-III.

Under the exact conditions of our rate measurements of the decalyl perbenzoate rearrangement, Denney⁸ has shown that the benzoate group is attached in the product IV by the same oxygen atom as in the starting material III. The mechanism of this rearrangement is ionic in the same sense and degree as that of solvolytic racemization of *threo*-3-

p-anisyl-2-butyl *p*-toluenesulfonate¹⁶ ($m = 0.57$ and 0.61 , respectively). Of the intermediates recognized for the latter reaction, only W-II, the "intimate ion pair," can possibly be involved in the decalyl perbenzoate rearrangement in view of the fact that the benzoate ion has never been free enough to make its oxygen atoms equivalent. The rearrangement of decalyl perbenzoate is thus in a class with those systems of Winstein which can be followed polarimetrically, this method being regarded as the way most likely to measure the primary ionizing process. It is consistent with this that the log k - Y plot is linear and of normal slope.

The shape of the log k - Y plot for *t*-butyl pertosylate is strongly reminiscent of the Winstein "special salt effects," in which the linear part of the curve above 0.03 M is believed to correspond to conditions where the solvent-separated ion pair W-III is converted into solvolysis products essentially as fast as it is formed. The drop below the line is then caused by a certain fraction of ion pair return which can be eliminated by small amounts of salts producing rapid intervention and realignment in W-III. In solvolysis this effect has never been noted as due purely to solvent variation; in the many dependences of ionization rate upon solvent composition, the solvent change has not been observed to shift the fraction of return in a way causing any gross deviation from the m - Y linear free energy relationship.

If the present case is analogous to the solvolyses, we seem to have only two possible interpretations. First, the line of log k vs. Y which has slope 0.44 may correspond as in the case of decalyl perbenzoate to the earliest stage of ionization, the formation of a W-II intermediate, which in the more aqueous media is becoming separated immediately with resulting disruption of the peroxide function. In this case the poorer solvating power of the low-water solvents may be permitting internal return which in this case does not form an isomer, but rather re-forms *t*-butyl pertosylate and drastically reduces the fraction of the initial ionization which leads to destruction of peroxide.

The second possibility is that, unlike the case of decalyl perbenzoate, the line of steep slope for *t*-butyl pertosylate corresponds to ion-pair return from W-III being permitted by the low-water solvent mixtures. In such a case there is no reason why neutral salts should not produce an effect like that observed with solvent change, a true "special salt effect" in the Winstein sense.

Salt Effects

Figures 4 and 5 show the effect upon the rate constant of adding various concentrations of different salts in anhydrous methanol. Up to 0.1 M , that is within and beyond the range of concentration where classical salt effects and Winstein special salt effects are to be sought, there is no effect on the rate from sodium or lithium perchlorate, lithium chloride, sodium tosylate or ammonium nitrate. At 0.2 M there is a rise, steeper for the perchlorates than for lithium chloride, to a maximum at about 0.3 M for the former and 0.4 M for

(14) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *THIS JOURNAL*, **78**, 328 (1956), and previous papers there cited.

(15) The prefix "W" is used here to distinguish Winstein's general notation from the standard Roman numerals designating structures in this paper.

(16) S. Winstein and C. G. Robinson, *THIS JOURNAL*, **80**, 169 (1958).

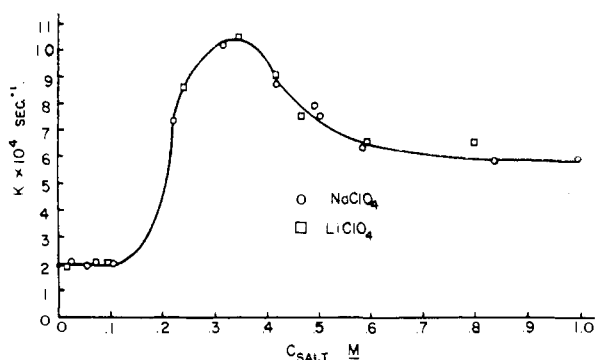


Fig. 4.—Effect of added sodium perchlorate (circles) and lithium perchlorate (squares) upon the rate constant for disappearance of peroxide titer in *t*-butyl pertosylate in anhydrous methanol at 4.50°.

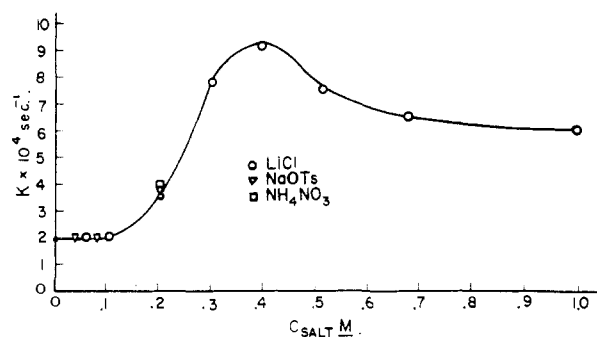


Fig. 5.—Effect of added lithium chloride (circles), sodium *p*-toluenesulfonate (triangles) and ammonium nitrate (squares) upon the rate constant for disappearance of peroxide titer in *t*-butyl pertosylate in anhydrous methanol at 4.50°.

the latter, beyond which the rate again declines up to 1 *M*, the highest salt concentration investigated. The maximum rate constant in the presence of sodium and lithium perchlorates is almost exactly equal to the extrapolated value for methanol in Fig. 3, namely, five times the rate constant in the absence of salt. The maximum for lithium chloride is about 10% less than this.

Figure 6 shows the effect of lithium chloride on the rate constant in various water-alcohol mixtures. With a mole fraction of water equal to 0.0114 the curve is similar to that in pure methanol; with increasing water content of the medium the effect of salt becomes rapidly less until, when the mole fraction of water is equal to 0.0545, lithium chloride up to 1 *M* has no effect whatever. Thus the salt effect exists only for solvent mixtures to the left of the inflection points in the rate-composition curves of Figs. 2 and 3.

This fact, and the coincidence of the maximum rate produced by salt in methanol with the extrapolated rate from the *Y*-log *k* curve, are suggestive parallels between the pertosylate system and the solvolyses which show special salt effects. However, our system obviously lacks the high sensitivity to ionic reagents which characterizes the W-III ion-pair return phenomenon of Winstein and co-workers, and this appears to us a serious argument against the second interpretation suggested above.

Pending the outcome of further investigation, we suggest that this system represents the previously unobserved case of internal return from W-II causing a deviation from the *Y*-log *k* linear free energy relationship, the internal return being eliminated when, either by a sufficient water content or by a high salt concentration, the ionizing power of the solvent is sufficiently increased above that of pure methanol. It seems likely that the distinguishing characteristic of *t*-butyl peresters in

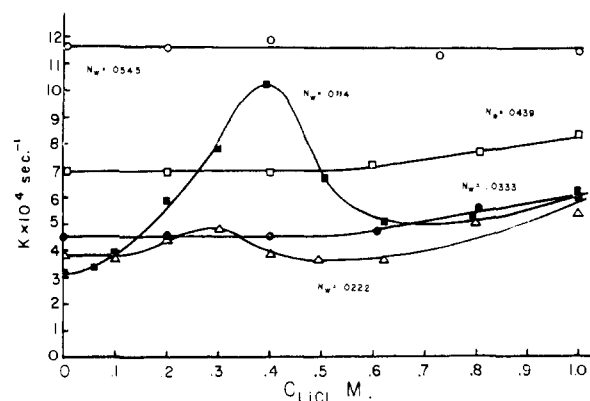


Fig. 6.—Effect of added lithium chloride on the rate constant for disappearance of peroxide titer in *t*-butyl pertosylate at 4.50° in several water-methanol mixed solvents: ■, $N_w = 0.0114$; △, $N_w = 0.0222$; ●, $N_w = 0.0333$; □, $N_w = 0.0439$; ○, $N_w = 0.0545$; N_w = mole fraction of water.

comparison with their decalyl counterparts is the low migration aptitude of the methyl group, which prolongs the lifetime of the positively polarized *t*-butoxy groups in comparison to any other tertiary alkoxy system.

Experimental

Preparation of Peresters. (a) *t*-Butyl Hydroperoxide.—Commercial *t*-butyl hydroperoxide (Lucidol, 67%) was fractionated through a 20-in. Vigreux column under vacuum. A large forerun consisting mostly of water and di-*t*-butyl peroxide was first taken off, and the hydroperoxide was then distilled over: b.p. 48° (28 mm.), f.p. 2°, n_D^{25} 1.4000; lit.¹⁷ m.p. 3.8–4.8°, n_D^{20} 1.4013.

(b) Sulfonyl Chlorides.—*p*-Bromobenzene-, *p*-chlorobenzene- and *p*-toluenesulfonyl chlorides (Eastman Kodak Co. white label) were recrystallized from ether in powdered Dry Ice. The ethereal solutions were washed with 10% sodium hydroxide until colorless and dried over anhydrous sodium sulfate before the recrystallization. The alkali wash is essential to good yields of perester in these cases. *p*-Methoxybenzenesulfonyl chloride was prepared by the method of Morgan and Cretcher,¹⁸ and recrystallized as described above. Benzenesulfonyl chloride (Eastman white label) was used directly.

(c) Pyridine.—The pyridine used as esterifying agent was refluxed for 24 hours over CaH_2 , and distilled through a helices-packed, vacuum-jacketed column, b.p. 114°. It was stored over barium oxide.

(d) *t*-Butyl *p*-Toluenepersulfonate (*t*-Butyl Pertosylate).—The preparation of this perester is described in detail; the same method was used to synthesize the other peresters. Twenty grams of tosyl chloride was dissolved in 150 g. of pyridine and the straw-colored solution chilled to –25° in the freezer; 10 g. of *t*-butyl hydroperoxide was added, and the solution was let stand for 14 hours at –25°. A white

(17) N. A. Milas and D. M. Surgenor, *THIS JOURNAL*, **68**, 206 (1946).

(18) M. S. Morgan and L. H. Cretcher, *ibid.*, **70**, 375 (1948).

precipitate formed, and the solution turned greenish-yellow. The mixture was poured on a slurry of ice and HCl with vigorous stirring, whereupon a coarse white precipitate formed. The crystals were filtered off and taken up in a petroleum ether-ether mixture; this solution was decanted from a small quantity of insoluble brown oil, dried for about 10 minutes over sodium sulfate, and chilled to -80° in powdered Dry Ice. A second recrystallization from petroleum ether-ether gave the perester as a free-flowing white powder, m.p. $36.5-37.0^{\circ}$ dec., yield 65-75%.

The perester is stable at room temperature for about 5 to 9 minutes, after which time it may decompose violently to give a black tar. It can be stored for about 4 to 6 weeks in a desiccator at -25° .

The glassware for the esterification reaction must be thoroughly dried; otherwise the yields are very low. *Anal.* Calcd.: O active, 6.55; S, 13.12. Found: O active, 6.62, 6.60, 6.69; S, 13.15.

(e) *t*-Butyl *p*-methoxybenzenepersulfonate, m.p. 47° (expl.), yield 80%. *Anal.* Calcd.: O active, 6.23, 6.25; S, 12.32. Found: O active, 6.20, 6.25; S, 12.56.

(f) *t*-Butyl *p*-bromobenzenepersulfonate, m.p. $40-41^{\circ}$ (expl.), yield 2-5%. *Anal.* Calcd.: O active, 5.17; S, 10.37. Found: O active, 5.07, 5.11; S, 10.42.

(g) *t*-Butyl *p*-chlorobenzenepersulfonate, m.p. $30-30.5^{\circ}$ (expl.), yield 2-6%. *Anal.* Calcd.: O active, 6.03; S, 12.11. Found: O active, 5.90, 6.00; S, 11.97.

(h) *t*-Butyl benzenepersulfonate, colorless liq., n_D^{25} 1.4629, yield 34%. *Anal.* Calcd.: O active, 6.98; S, 13.98. Found: O active, 7.17, 6.92; S, 14.07.

(i) **Attempted Synthesis of *t*-Butyl *p*-Nitrobenzenepersulfonate.**—No perester was obtained using the pyridine condensation method. Acidification of the pyridine reaction mixture gave only a yellow aqueous solution of the free sulfonic acid. A qualitative test was run to see whether any perester does form in this system. *t*-Butyl hydroperoxide was added to a pyridine solution of sulfonyl chloride at room temperature with no cooling. The reaction mixture became quite warm and a precipitate formed, but the solution remained clear. (The precipitate was too hygroscopic to characterize, but it gave a yellow aqueous solution as it must if it consisted in part of pyridinium *p*-nitrobenzenesulfonate.) This test applied to the synthesis of the other peresters results in a violent reaction, with the solution turning hot and black from the decomposition of perester.

The reason for the failure of this synthesis is probably the rearrangement of the perester as it forms. Evidence for this is provided by the isolation of acetone 2,4-DNP from the reaction mixture in 27% yield.

In an attempt to prevent the rearrangement by using less polar solvents, pentane, ether or mixtures of the two were tried as reaction media. In most cases only starting material was recovered, and in no case was any perester found.

(j) **Elemental Analyses of the Persulfonates.**—The *t*-butyl arylpersulfonates are all too unstable to permit analysis of carbon and hydrogen. The peroxidic or active oxygen was determined by the standard iodometric method. The sulfur content was determined as follows. The perester sample (about 100 mg.) was weighed into a small round bottomed flask, dissolved in concd. HNO_3 , and the solution refluxed for 4 hours. The solution was then evaporated almost to dryness after which 0.5 g. of KNO_3 and 0.5 g. of NaNO_3 was added. The mixture was fused and heated until a clear melt was obtained. The white nitrate salt was twice evaporated to dryness with concd. HCl to remove NO_3^- ion. The resulting chloride salt was taken up in water, acidified with four drops of 6 N HCl, and the BaSO_4 precipitated by addition of BaCl_2 solution. The precipitate was digested for one hour on the steam-bath, and then filtered on a previously weighed sintered glass crucible. The precipitate was dried for 24 hours at 110° and weighed.

Product Studies. (a) Persulfonates in Methanol.—The perester sample (100-200 mg.) was weighed into a 10-ml. erlenmeyer flask and dissolved in 6-7 ml. of methanol. The samples were chilled in powdered Dry Ice before weighing; this treatment and the use of small samples made the weighing procedure perfectly safe. The solutions were let stand overnight in the dark. A single solution was used *in toto* for one determination. The peroxide content, which always turned out to be nil, was tested by the analytical method described below. The sulfonic acid content was determined by titration with standard base to a brom thymol blue end-point in erlenmeyer flasks of known weight. The

titration solution was then evaporated to dryness; the salt was dried for 24 hours at 110° and weighed. The moles of salt were calculated using the molecular weight of unhydrated salt.

The acetone content of the solution was determined gravimetrically as the 2,4-dinitrophenylhydrazine using a slight modification of the method of Shriner, Fuson and Curtin.¹⁹ The 2,4-DNPH reagent was made up by adding 3 ml. of concd. H_2SO_4 to 0.4 g. of 2,4-dinitrophenylhydrazine, and then adding 13 ml. of water slowly to give a warm yellow solution. Five drops of ethanol was added to clear up any turbidity still present. The warm reagent was then added to sample solution which had been washed with a little methanol into a 50-ml. erlenmeyer. The precipitate of acetone 2,4-DNP formed almost immediately. The mixture was let stand for about 4 hours at room temperature to complete the precipitation, and the acetone 2,4-DNP was filtered on a weighed sintered glass crucible. The precipitate was washed with 60 to 80 ml. of 10% H_2SO_4 and then with 100 ml. of water. The precipitate was dried for 30 minutes in an oven at 100° to 105° and weighed. This time sufficed for complete drying and longer times led to decomposition. The melting points of the acetone 2,4-DNP thus obtained were usually $124-126^{\circ}$, the lowest observed being 122° (pure acetone 2,4-DNP has m.p. 126°).

(b) ***t*-Butyl Hydroperoxide in Methanol.**—The sample of *t*-butyl hydroperoxide was dissolved in 10 ml. of dry methanol and the reaction tube was then sealed off with a flame. The sealed tube was placed inside a steam-bath for 5 days with the steam valve wide open. A control run showed that all the hydroperoxide had decomposed at the end of this time. The tube was chilled in the freezer before opening. The contents were treated with 2,4-dinitrophenylhydrazine reagent and the precipitate dried and weighed as described above. Each sample had m.p. $166-167^{\circ}$ after one recrystallization from ethanol.

Run	<i>t</i> -BuOOH, mmoles	$\text{CH}_3\text{O}-2,4\text{-DNP}$, mmoles	% ^a
1	1.278	0.934 ^b	73.1
2	3.323	2.183 ^c	65.7

^a Based on *t*-butyl hydroperoxide. ^b M.p. $160-163^{\circ}$, mixed m.p. with authentic formaldehyde 2,4-DNP, (m.p. $166-167^{\circ}$), $166-167^{\circ}$. ^c M.p. $159-163^{\circ}$, mixed m.p. with authentic formaldehyde 2,4-DNP, $166-167^{\circ}$.

(c) ***t*-Butyl Pertosylate in Pyridine.**—Three grams of *t*-butyl pertosylate was dissolved in 25 ml. of dry pyridine and the solution was let stand two hours at room temperature in the pot of a distillation apparatus. All glassware used had been dried at 140° for 24 hours. The solution was then heated gently on the steam-bath and about 1 ml. of liquid distilled over. This was taken up in 20 ml. of CCl_4 , which had been dried over Drierite, and about one-third of this volume of solution was redistilled from Drierite to a receiver also containing Drierite. The infrared spectrum of this solution was taken about 30 minutes after the final distillation. This spectrum and that of pure isopropenyl methyl ether (2-methoxypropene) prepared by Crocker and Hall²⁰ were identical. Our solution showed an acetone spectrum superposed upon that of isopropenyl methyl ether; the intensity of the acetone bands increased at the expense of the ether spectrum even on standing in a stoppered flask over Drierite for five hours, indicating a strong susceptibility of the unsaturated ether to hydrolysis by very small amounts of water.

Kinetic Procedure for the Persulfonates. (a) Solvents.—Anhydrous methanol (Merck reagent grade) was refluxed overnight over CaH_2 and distilled through a 20-in. Vigreux column. A middle cut, b.p. 65.0° , was used. Some samples were distilled in a slow stream of nitrogen, but as this procedure had no effect on the rates measured it was discontinued.

Aqueous methanol solutions were made up by diluting known amounts of water to the mark in a volumetric flask with methanol. The water was measured out from a mi-

(19) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 219.

(20) H. P. Crocker and R. H. Hall, *J. Chem. Soc.*, 2052 (1955). The authors are indebted to Dr. A. R. Phillpotts of the Distillers Co. Ltd. for the infrared spectrum of pure isopropenyl methyl ether.

croburet calibrated gravimetrically at room temperature (25°). Final volumes were taken at 25°. The weight of methanol added then was taken to determine the mole fractions of the components.

Solutions with added salt were made up directly as used, final volumes being taken at 25°. The reported concentrations of salt are corrected to 0°. All salts used were of reagent grade. The perchlorate salts were dried *in vacuo* over P₂O₅ at 78°.

(b) **Analysis Mixture.**—The following reagents were used directly: acetic anhydride (Merck reagent grade), acetic acid (du Pont C.P. reagent), isopropyl alcohol (Eastman white label) and potassium iodide (Merck reagent grade).

(c) **Determination of the Rate Constants.**—Since the peresters are too unstable to weigh out, an estimated amount of perester was dissolved in 50 to 80 ml. of the methanolic solution which had been left for at least two hours in the constant temperature bath. The kinetic measurement was started as soon as the dissolution was complete; 5-ml. aliquots were taken in rapid discharge pipets and the time recorded at the end of the discharge. Prechilling of the pipets proved unnecessary. The first aliquot defined zero time. The reaction solution was added to 3 g. of potassium iodide suspended in a mixture of 10 ml. of acetic acid, 6 ml. of acetic anhydride and 15 ml. of isopropyl alcohol. The flask was swirled for 50 to 80 seconds, 35 ml. of water was added and the iodine liberated was titrated with standard thiosulfate solution. The disappearance of the yellow color defined the end-point. For the reaction solutions of high water content, 30 to 50 seconds of swirling was found adequate. Within a given run, the period of swirling was always kept constant.

The following procedure was used to exclude oxygen from the analytical mixture. The acid-anhydride-isopropyl alcohol mixture was flushed for about 1 hour with nitrogen. The potassium iodide was added just before the determination and the flask sealed with a glass stopper. Just before the aliquot was pipetted into the mixture, a small piece of Dry Ice was dropped into the flask, both to prevent the diffusion of air into the flask and to flush out any oxygen picked up by the methanol solution. The flask was left stoppered during the reaction of perester with iodide, the pressure from CO₂ liberated by the piece of Dry Ice being released when necessary. The water added just prior to titration was flushed with nitrogen for at least one hour before use. A piece of Dry Ice was added to the flask during the titration. Under these conditions, blank solutions liberated no iodine for 15 minutes, and the determinations always were finished within 5 minutes.

Despite these precautions, oxygen did find its way into some of the analytical mixtures, and some values for perester concentration were found which were high by 50% or more. These values were not used. On a few occasions, the run was rendered useless by this difficulty. The use of acetic anhydride, which is necessary for the rapid quantitative reaction of the perester with iodide ion, sensitizes the iodide to attack by oxygen. Whereas suspensions of potassium iodide in acetic acid remain colorless for several minutes in the presence of air, those containing acetic anhydride turn yellow in about a minute. In some of the early runs, occasional determinations of perester concentration were low by a factor of two or more. This was not encountered if the mixtures were swirled vigorously. Errors from autoxidation of iodide were in general so gross as to make them immediately obvious. The main source of error in these determinations was indistinct end-points, sometimes complicated by rapid fading of the end-points.

Since analysis of the first aliquot defining zero time was subject to the same errors as subsequent aliquots, log (perester concentration) was plotted directly *versus* time, and the rate constant was determined graphically from the slope of the line through the points. Eight points were usually taken during a given run; for the very fast runs only four to six could be taken, and for the slower runs ten were taken. The extent of reaction during a given run varied from 60 to 90%.

Kinetics of the Rearrangement of Decalyl Perbenzoate. (a) **Decalyl Hydroperoxide.**—One kilogram of decalin (Eastman pract. grade) was purified over silica by the method of Cope and Holtzman.²¹ It was then heated on the steam-bath to about 95°, after which the oxygen was bubbled in

through a sintered glass plate. The solution was stirred vigorously and the heating continued throughout the oxidation. The initiator used was azoisobutyronitrile (m.p. 102–103° dec.) which was added in 2-g. lots at intervals of 10 to 12 minutes. After the last lot of initiator had been added, the resulting pale green liquid was cooled in ice and extracted with 12% aqueous NaOH. The addition of base turned the solution red; the red color, however, came out in the aqueous layer, though some trouble was had with emulsification. The now colorless solution was dried over Na₂SO₄ and the decalin removed under vacuum. After one day in the ice-box most of the residue crystallized; yield, after two recrystallizations from hexane, 7.0 g., m.p. 94°. The sirupy mother liquor from the first crystallization gave another 2.0 g. (after recrystallization) of material after four days standing in the ice-box. The conversion in this procedure is lower than in that of Cope and Holtzman, but the procedure itself is far more convenient.

(b) **Decalyl perbenzoate** was prepared by the method of Cope and Holtzman and recrystallized twice in a Dry Ice-bath from methanol-ether, m.p. 67.0°.

(c) **Kinetic Procedure.**—The mixtures of aqueous methanol were made up in the same way as those used in the persulfonate runs. The kinetics of the rearrangement was followed by the analytical method of Bartlett and Kice.⁶ The rate constants were evaluated graphically from plots of log (perester concentration) *versus* time. Zero time was defined as the first aliquot taken. This method was necessary in the solvent mixtures of high water content in which the perester would dissolve only slowly, and was adopted for all the runs in order to maintain a standard procedure. The reaction solvent was kept for at least one hour in the constant temperature bath (25.03 ± 0.02°) before a run.

(d) **Side Reaction of Decalyl Perbenzoate.**—Samples of the perester were weighed into volumetric flasks, dissolved in methanol, the required amount of water added, and the solution made up to the mark with methanol. The flasks were placed in the 25.0° constant temperature bath and left for approximately 10 half-lives. The volume was checked after the first half-hour and enough methanol added to bring the solution back up to the mark. (The solutions warm up on addition of water.) After 10 half-lives, the free benzoic acid was titrated with aqueous NaOH to a phenolphthalein end-point. The base was standardized against a methanolic solution of benzoic acid of such normality as to require about the same volume as the experimental solutions. The fraction of benzoic acid produced was constant, in agreement with Goering and Olson.⁷

Solvolysis of *t*-Butyl Chloride. (a) *t*-Butyl Chloride.—

TABLE I

Mole frac. H ₂ O	$k \times 10^6, \text{sec.}^{-1}$ ^a	Y (obs.) ^b	Y (calcd.) ^c
0	0.752 ± 0.016 ^d	-1.090	-1.079
0	.753 ^e	-1.090	-1.079
0.0114	.810 ± 0.005	-1.058	-1.041
.0222	.838 ± .008	-1.043	-1.003
.0333	.891 ± .003	-1.017	-0.965
.0439	.960 ± .015	-0.984	-.927
.0545	1.21 ± .02	-.884	-.888
.0568	1.22 ^f	-.880	-.881
.065	1.28 ^f	-.850	-.851
.0813	1.373 ± .003	-.829	-.792
.103	1.72 ± .02	-.731	-.710
.124	2.18 ^f	-.628	-.629
.125	2.20 ± .02	-.624	-.625
.150	2.77 ± .03	-.524	-.529
.200	4.10 ± .06	-.354	-.327
.201	4.64 ^g	-.301	-.325
.240	6.81 ^f	-.133	-.160
.242	6.16 ± .04	-.177	-.152
.282	9.16 ± .10	-.005	-.020

^a Temp. 25.03 ± 0.02° for these measurements. ^b Based on $k = 9.26 \times 10^{-6} \text{ sec.}^{-1}$ for 80% ethanol, $Y = 0.13$

^c Calculated from equation $Y = -1.079 + 3.362N_W + 2.173N_W^2 - 0.944N_W^3$. ^d Duplicate determinations; error limits shown are average deviations. ^e Data of Fainberg and Winstein.¹³ ^f Data of Cropper, Spieth and Olson.²²

(21) A. C. Cope and G. Holtzman, *This Journal*, **72**, 3062 (1950).

t-Butyl chloride (kindly supplied by S. J. Tauber) was fractionally distilled from CaO, a center cut of b.p. 51.0° being taken, n_D^{20} 1.3854, lit.¹³ n_D^{20} 1.3855. The mixtures of aqueous methanol were made up in the same way as those used for the persulfonate runs.

(b) **Kinetic Procedure.**—The solvolysis was carried out in sealed tubes and followed by the appearance of HCl, using a titrimetric method of Fainberg and Winstein. In this method, the contents of the tube were washed into 25 ml. of acetone and titrated with methanolic NaOH to a brom phenol blue end-point (very sharp color change from yellow to green). The methanolic NaOH was standardized against standard HCl under the same conditions. The tubes held 5-ml. aliquots for the most part, 10-ml. aliquots being used at the beginning of the reaction when the acid concentration was still low. The solvent was kept in the constant temperature bath at least an hour before each run. Zero time was taken at the addition of *t*-butyl chloride to the solvent. Immediately after the *t*-butyl chloride was mixed with the solvent, the infinity point was taken by pipetting three or four 5-ml. aliquots into 35 ml. of water and letting the resulting solution stand for 4 to 5 hours. The acid content was determined by titration with methanolic NaOH to a phenolphthalein end-point, the base having been standardized against standard HCl under the same conditions. Fainberg and Winstein used brom thymol blue indicator, but

this proved unsatisfactory here since the color change was not in the least sharp. Of a series of other indicators tried, only phenolphthalein gave an acceptable precision of 0.1 ml. in 15 to 20 ml. of titrant used. The rate constants were evaluated graphically from a plot of $\log(A_\infty - A)$ versus time, where A_∞ is the "infinity" acid concentration and A the acid concentration at time t . Each plot had 8 to 10 points to determine the line.

Y-Values.—Because of the increasing reference value of the rate constants for solvolysis of *t*-butyl chloride, presented in Table I are the new values for the methanol-water system of mixed solvents, together with a comparison with the results for the less closely spaced solvent mixtures reported by Fainberg and Winstein¹³ and by Cropper, Spieth and Olson.²² The values calculated from the empirical equation of Fainberg and Winstein are also shown.

Acknowledgment.—This investigation was supported by a grant from the Higgins Fund of Harvard University, and by a Fellowship from the National Institutes of Health to the junior author.

(22) W. H. Cropper, F. Spieth and A. R. Olson, *THIS JOURNAL*, **76**, 6248 (1954).

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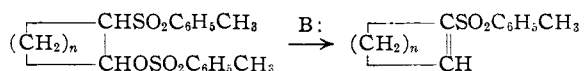
cis Elimination Mechanisms: The Base-catalyzed Deuterium Exchange of Cycloalkyl *p*-Tolyl Sulfones

BY JOSEPH WEINSTOCK,¹ JAMES L. BERNARDI AND RALPH G. PEARSON

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The rates of base-catalyzed exchange of deuterium for hydrogen alpha to the sulfone in cyclopentyl and cyclohexyl *p*-tolyl sulfone have been measured at several temperatures, and activation energies for the reaction obtained. Comparison of these rates with those of the base-catalyzed elimination reactions of the corresponding *trans*-sulfone tosylates which undergo *cis*-elimination shows that deuterium exchange is from 10⁻³ to 10⁻⁶ as rapid, and thus that carbanion formation cannot be the rate-determining step in the elimination reactions. It was found that for deuterium exchange the cyclopentyl system reacts about 1.5 times faster than the cyclohexyl system, while in the *cis* elimination reactions of *trans*-sulfone tosylates the ratio is about 6. This suggests that there is no relief of strain in the transition state in the cyclopentyl system when going to the anion, but that there is relief of strain in going to the transition state leading to olefin. Hence, there is partial double bond formation in the transition state leading to elimination and a free carbanion intermediate seems excluded.

In a study of the base-catalyzed elimination reactions of *cis*- and *trans*-2-(*p*-tolylsulfonyl)-cycloalkyl *p*-toluenesulfonates² (I) we have found that although the *trans* elimination using hydroxide ion as the base goes 400 times faster than *cis* elimination in the cyclohexyl system, and 20 times faster in the cyclopentyl system, both *cis* and *trans* eliminations are subject to general base catalysis. This indicated that no carbanion which existed long enough to revert to sulfone tosylate was present as



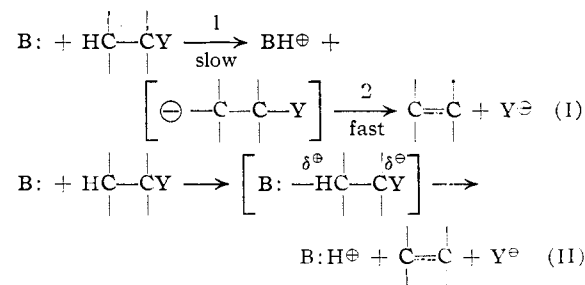
Ia, *trans*-cyclohexyl
Ib, *trans*-cyclopentyl
Ic, *cis*-cyclohexyl
Id, *trans*-cyclopentyl

an intermediate, and that removal of a proton was involved in the rate-determining step. However, this work did not show whether a short lived carbanion was involved as an intermediate (mechanism

(1) Research and Development Division, Smith, Kline and French Laboratories, Philadelphia 1, Pa. This paper was presented at the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pa., February 5, 1958.

(2) J. Weinstock, R. G. Pearson and F. G. Bordwell, *THIS JOURNAL*, **78**, 3468, 3473 (1956).

I) or if the reaction was concerted in the sense that the removal of the proton was made more facile by the simultaneous departure of the leaving group (mechanism II).



Other workers in this field³⁻⁵ have suggested that the results previously obtained would be consistent with mechanism I^{3,4} or mechanism II in which the C-Y bond has barely begun to break. The present work was undertaken as part of an effort to obtain evidence concerning the extent of concertedness, if any, of the elimination reactions

(3) H. L. Goering, D. I. Relyea and K. L. Howe, *ibid.*, **79**, 2502 (1957).

(4) S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957).

(5) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).