the molar absorbances of the ester, cation and molecular species being determined at a given wave length and temperature, the value of ϵ_M being corrected as described above. The wave lengths chosen were located at the peaks of the long wave length bands where the values of ϵ_{cation} are small. It was found practical to substitute the value ϵ_{anion} for ϵ_{ester} in a number of cases where the esters were very slightly soluble in water.

Summary

We have reached the following conclusions: 1. The Wegscheider assumption that the inductive effect of a COOH group is equal to that of a $COOC_2H_5$ group is invalid for substituted phenylglycines. Zwitterion ratios based on this assumption are suspect and should be checked by alternate criteria. 2. The proportion of zwitterions in aqueous solution is governed mainly by the effect of the substituent on the pK_a of the anilinium group, and can vary from a small fraction up to 90% in changing the substituent from *m*-NO_2 to *p*-OCH_3. 3. The presence of side chains with substantial $-I$ character attached to the nitrogen atom has little influence on the intensity of *m*- and *p*-substituent effects on the $-NH_2R^+$ ionization, the Hammett reaction constants being similar for four reaction series in which R may be H, CH_2COOH, CH_2COOEt and CH_2COO^-. 4. The presence of a positive constant term in the Hammett equations relating to the NH_2R^+ ionization is considered to indicate a different I/M ratio of the components of the substituent effect in anilines as compared with that in benzoic acids. 5. The transmission of the inductive effects of ring substituents to functional groups *via* side chains is related to the polarizabilities of the intervening groups, the efficiency decreasing in the sequence $NH > CH_2 > NH_2^+$.

Acknowledgment.—We acknowledge with thanks the microanalytical determinations carried out by Dr. E. Challen.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Anchimerically Accelerated Bond Homolysis. III.[1] Polar and Geometric Factors Influencing the Radical Decomposition of *t*-Butyl *o*-Phenylthioperbenzoate

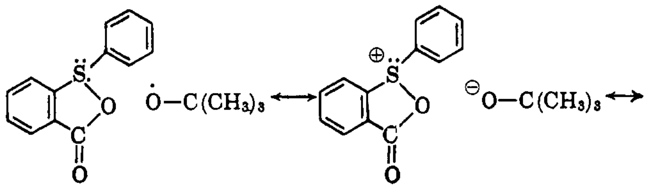
BY D. L. TULEEN,[2] W. G. BENTRUDE[2] AND J. C. MARTIN

RECEIVED JANUARY 9, 1963

The susceptibility of the rate of thermal decomposition of *t*-butyl *o*-phenylthioperbenzoate to the effects of substituents, solvent ionizing power and added salt indicates that a large contribution to the transition state for this homolysis is made by dipolar structures in which sulfur bears a positive charge. Further evidence is presented that the products of this decomposition are free radicals. Rates of decomposition of geometrically restricted model compounds indicate that homolytic decomposition may be anchimerically assisted by neighboring sulfur only when it is possible for the groups attached to sulfur to attain an approximately tetrahedral configuration. The results are compatible with a transition state, described rather well by structure II, in which the bonding to sulfur is very similar to that in a sulfonium ion.

Many radical reactions resemble heterolytic processes to a considerable degree.[3] The effects of *m*- and *p*-substituents upon the rates of the thermal decomposition of benzoyl peroxides,[4,5] *t*-butyl perbenzoates[6] and phenylperacetates[7] are, for example, correlated by the Hammett σ–ρ relationship. Even for reactions showing appreciable polar substituent effects the separation of charge in the transition states is usually not large enough to be reflected in an unambiguous dependence of rate on solvent polarity. Rates of certain radical reactions have, indeed, been shown[8–10] to vary markedly with solvent. A clear-cut correlation with solvent ionizing power has not, however, been made prior to this work.

It has been proposed[1] that the transition state for the anchimerically assisted homolysis of *t*-butyl *o*-phenylthioperbenzoate may be represented by structures I and II. The importance to the transition state of the contribution made by dipolar structure II, or the closely analogous structure III, has been evaluated by an examination of the response of the rate of decomposition of this perester to the effects of substituents, of the ionizing power of the solvent, of added salt and of geometric restraint (in closely related series of model compounds). In a previous communication[11] we presented evidence that this decomposition is sensitive to changes in the ionizing power of the solvent. In this paper results are presented which confirm and extend this view.



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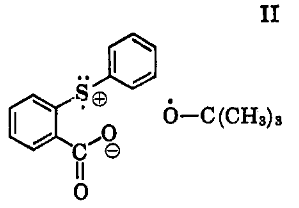

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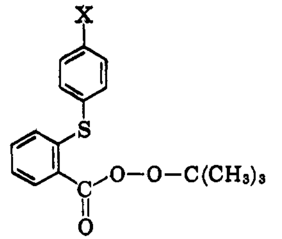

IV

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[1] For part II see W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962).

[2] Taken from the Ph.D. Theses of D. L. Tuleen, Univ. of Ill., July, 1962, and W. G. Bentrude, Univ. of Ill., June, 1961.

[3] For discussions see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, Chap. XII.

[4] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

[5] A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

[6] A. T. Blomquist and I. A. Berstein, *ibid.*, **73**, 5546 (1951).

[7] P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960).

[8] J. E. Leffler and W. B. Bond, *ibid.*, **78**, 335 (1956).

[9] W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961).

[10] R. C. Lamb, F. F. Rogers, G. D. Dean and F. W. Voight, *J. Am. Chem. Soc.*, **84**, 2635 (1962).

[11] J. C. Martin, D. L. Tuleen and W. G. Bentrude, *Tetrahedron Letters*, 229 (1962).

TABLE I

DECOMPOSITION OF IV IN CHLOROBENZENE

X	T, °C.	$k \times 10^5$, sec.$^{-1}$[b]	H^+, kcal./mole	S^+, e.u.
CH_3O[a]	34.07	12.7 ± 0.4	20.3 ± 0.3	−10.3 ± 1.6
	50.30	68.3 ± 2.4		
	64.57	284 ± 3		
Cl[a]	40.0	3.89 ± 0.06	22.4 ± 0.3	−7.2 ± 1.6
	50.3	12.6 ± 0.2		
	70.1	99.8 ± 10.3		
NO_2[c]	50.20	3.46 ± 0.03	22.0 ± 0.2	−10.0 ± 1.3
	50.20[a]	3.45 ± .06		
	67.67	20.3 ± .4		
	83.63	94.7 ± .01		

[a] 0.2 *M* in styrene, to inhibit induced decomposition; concentration of perester, 0.030 *M*. [b] By the method of least squares. Uncertainties are expressed as standard deviations. Reactions were followed by observing the disappearance of the perester carbonyl absorption in the infrared spectrum. [c] Concentration of perester, 0.029 *M*.

Results

Substituent Effects.—Rate studies on the decomposition of substituted *t*-butyl *o*-phenylthioperbenzoates IV are summarized in Table I. A Hammett plot of these data yields a ρ for the reaction of −1.3.

The Effect of Solvent Polarity.—The first-order thermal decomposition of *t*-butyl *o*-phenylthioperbenzoate was studied in solvents possessing a wide range of polarity, at 25° and at 40°. The results of this study, with the dielectric constant, D, of each solvent, are listed in Table II.

TABLE II

DECOMPOSITION OF *t*-BUTYL *o*-PHENYLTHIOPERBENZOATE

		25°			40°		
		$k \times 10^4$, sec.$^{-1}$			$k \times 10^4$, sec.$^{-1}$		
Solvent	Dielectric[12-14] constant, D_{25}	By infrared[a]	By scavenger[b]	% trapping	By infrared[a]	By scavenger[b]	% trapping
Cyclohexane[c]	2.02	0.00985	0.0033	34	0.0686	0.024	33
Tetrahydrofuran	7.39		0.043		0.30 ± 0.004		
Chlorobenzene[c]	5.62	0.176			1.03	0.49	48
Nitrobenzene						.88	
Acetone	20.7	0.189 ± 0.003[g]	0.060	32	1.22 ± 0.02	.66	54
90% dioxane[d]	5.6	.474 ± .003	.46	98	2.40 ± .03		
t-Butyl alcohol	10.9[e]	.526 ± .012	.16	30	3.24 ± .06		
Acetonitrile	37.5[f]	1.01 ± .01	.66	66	5.44 ± .09	2.4	45
85% dioxane[d]		1.03 ± .01	. . .	. .			
Dimethyl sulfoxide	45	1.11 ± .02			6.02 ± 0.12		
80% dioxane[d]	10.7	1.38 ± .03	0.95	69	7.03 ± .09		
2-Propanol	18.3	1.33 ± .03	0.54	41	7.25 ± .10		
Ethanol	24.3	2.31 ± .02	1.2	52	16.5 ± .3	5.7	34
Methanol	32.6	8.21 ± .25	2.7	33	47.5 ± .4	10.4	22

[a] Rates followed by observing disappearance of the perester carbonyl absorption, infrared spectroscopy. [b] Rate is the average of runs following the zero-order disappearance of the absorption of the scavenger, galvinoxyl, at 570 mμ in the presence of a large excess of perester. [c] Infrared rates extrapolated from linear plot of ln k/T *vs.* $1/T$. All infrared rates except those denoted by *c* are from runs including 0.2 *M* styrene. [d] Aqueous dioxane, per cent by weight. [e] At 30°. [f] At 20°. [g] Analyzed in CCl_4 solution after removal of acetone.

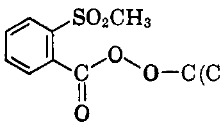
Rates were measured by two independent techniques, following perester concentration by infrared spectroscopy and following the rate of radical generation by a scavenger technique. Both methods gave results fitting a rate law first order in perester.

The radical scavenger, galvinoxyl,[7] was employed in the scavenger studies, observing the disappearance of the absorption at 570 mμ.

Bentrude and Martin have demonstrated[1] that atmospheric oxygen has no effect on the rate constant obtained by galvinoxyl scavenging of the perester-derived radicals. A scavenger blank was shown to be stable over the length of time required for the kinetic run in each of the solvents. A solution of *t*-butyl hydroperoxide in ethanol does not decolorize galvinoxyl under these conditions, ruling out a mechanism for radical generation involving solvolysis of the perester.

The addition of lithium perchlorate accelerates the rate of decomposition of *t*-butyl *o*-phenylthioperbenzoate in tetrahydrofuran. This positive salt effect is indicated in the results summarized in Table III.

Steric Effects.—The extent of sulfur participation in O–O bond homolysis in a series of *t*-butyl peresters was assessed by a comparison of the rates of decomposition with that of *t*-butyl perbenzoate VIII. The series included *t*-butyl *o*-methylsulfonylperbenzoate (V), *t*-butyl dibenzothiophene (VI) and *t*-butyl thioxanthone-4-percarboxylate (VII). The results are summarized in Table IV. Rate constants redetermined for VIII, using quantitative infrared analysis, are consistent with



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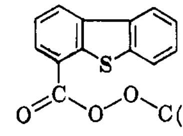

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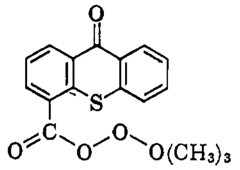

VII

TABLE III

DECOMPOSITION OF *t*-BUTYL *o*-PHENYLTHIOPERBENZOATE[a] AT 25° IN TETRAHYDROFURAN[b] WITH ADDED LITHIUM PERCHLORATE

	$k \times 10^5$, sec.$^{-1}$		
Salt	By scavenging	By infrared	Trapping, %
None	0.43		
0.0124 *M*	0.78		
.031 *M*	1.3	1.41 ± 0.03	92
.093 *M*	3.3	3.53 ± .08	93
.124 *M*	4.5	5.10 ± .30	88

[a] Perester concentration, 0.06 *M*. [b] With added styrene, 0.4 *M*.

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(12) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," U. S. Bureau of Standards Circular 514, 1957.

(13) F. E. Critchfield, J. A. Gibson and J. L. Hall, *J. Am. Chem. Soc.*, **75**, 6044 (1953).

(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950.

TABLE IV

DECOMPOSITION[a] OF *t*-BUTYL PERESTERS IN CHLOROBENZENE

Perester	T, °C.	P_0[b]	k, sec.$^{-1}$[c]
VIII	120.0	0.036[d]	$(1.31 \pm 0.05) \times 10^{-4}$
VIII	135.0	.051[d]	$(6.74 \pm .50) \times 10^{-4}$
VIII	150.0	.095[d]	$(3.12 \pm .10) \times 10^{-3}$
V	105.0	.052	$(6.68 \pm .50) \times 10^{-6}$
V	120.0	.063	$(5.57 \pm .25) \times 10^{-5}$
V	135.0	.060	$(2.76 \pm .08) \times 10^{-4}$
V	150.6	.051	$(2.05 \pm .03) \times 10^{-3}$
VI	105.0	.048	$(2.79 \pm .07) \times 10^{-5}$
VI	119.4	.026	$(1.29 \pm .03) \times 10^{-4}$
VI	135.1	.034	$(6.07 \pm .36) \times 10^{-4}$
VII	120.0	.073[d]	$(1.89 \pm .04) \times 10^{-4}$
VII	135.0	.070[d]	$(1.15 \pm .04) \times 10^{-3}$

[a] Followed by observing the perester carbonyl absorption in the infrared spectrum. [b] P_0 is initial perester concentration in moles/liter. [c] Rate constants and standard deviation determined by the method of least squares. [d] Contains 0.2 M styrene to minimize induced decomposition.

values determined titrimetrically by Blomquist and Ferris.[15]

The experimentally determined activation parameters are: for compound V, $\Delta H^{\ddagger} = 38$ kcal./mole, $\Delta S^{\ddagger} = 19.5$ e.u.; for compound VI, $\Delta H^{\ddagger} = 30.6$ kcal./mole, $\Delta S^{\ddagger} = 1.0$ e.u.; for compound VII, $\Delta H^{\ddagger} = 37.4$ kcal./mole, $\Delta S^{\ddagger} = 19$ e.u.; for compound VIII, $\Delta H^{\ddagger} = 34.1$ kcal./mole, $\Delta S^{\ddagger} = 10.0$ e.u.

In Table V are listed the relative rates of decomposition of each of these peresters, compared not only with *t*-butyl perbenzoate, but also with the two peresters which are thought to decompose through bridged transition states.[6]

TABLE V

THERMAL DECOMPOSITIONS OF *t*-BUTYL PERESTERS IN CHLOROBENZENE

Perester, *t*-butyl	Relative rate[a] at 120°
Perbenzoate (VIII)	1.0
o-Methylsulfonylperbenzoate (V)	0.4
Dibenzothiophene-4-percarboxylate (VI)	1.0
Thioxanthone-4-percarboxylate (VII)	1.4
o-Methylthioperbenzoate[1]	1300
o-Phenylthioperbenzoate (IV, X = H)[1]	2200

[a] Followed by observing the perester carbonyl absorption in the infrared spectrum.

Discussion

Radical Nature of the Decomposition.—The complex product mixture which results from the decomposition of *t*-butyl *o*-phenylthioperbenzoate in chlorobenzene has been discussed[1] in terms of its possible genesis by a radical mechanism through a transition state characterized by the canonical forms I, II and III. Radicals produced in the decomposition of the perester in a variety of solvents are scavenged by the free radical galvinoxyl.

Our knowledge of the variation of trapping efficiency with solvent (Table II) does not allow any clear-cut answers to the causes of scavenger inefficiency. The possibilities of (1) geminate reactions or (2) the inability of galvinoxyl to react with all radicals which avoid the geminate reactions and become kinetically free were considered earlier,[1] and remain possibilities.

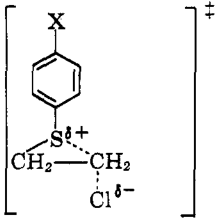
The possibility exists that in certain solvents the apparent first-order rate constant determined by infrared spectroscopy includes some radical chain-induced decomposition which is not inhibited by styrene. The rate constant determined by scavenging might then be appreciably less than the rate constant determined by the infrared technique. If such an explanation were valid, the induced decomposition would need to be most prevalent in cyclohexane, acetone and alcohols, and absent in 90% aqueous dioxane. Such behavior would be quite different from the results obtained in studies of the induced decomposition of benzoyl peroxide, for which induced decomposition was found to be prevalent in dioxane, relatively unimportant in cyclohexane and much more important in ethanol than in methanol.[16]

Linearity in plots of log k/T *vs.* $1/T$ for the decomposition of *t*-butyl *o*-phenylthioperbenzoate in cyclohexane and chlorobenzene seems to render improbable a mechanism for decomposition involving competition between radical and ionic pathways.[1] It does not rule out a mechanism involving a rate-determining ionization to an intermediate which can react to give products by competing ionic and radical pathways. If the relative rates of the two pathways in such a mechanism were sensitive to changes in solvent polarity, this sensitivity would be reflected in a dependence of product composition upon solvent polarity. The fraction of the rate constant accounted for by the use of the scavenger, as seen from Table II, is not at all correlated with solvent polarity. This seems to militate against any major contribution from an ionic reaction.

The generation of *t*-butoxy radicals in solvents from which hydrogen atoms are not readily abstracted by electronegative radicals characteristically yields a mixture of *t*-butyl alcohol and acetone. The fact that the decomposition of *t*-butyl *o*-phenylthioperbenzoate in acetic acid yields approximately 15% of acetone (isolated as the 2,4-dinitrophenylhydrazone) may therefore be taken as evidence for the formation of *t*-butoxy radicals even in this highly polar solvent. Decomposition under similar conditions in the less polar solvent chlorobenzene yields a comparable amount of acetone (about 30%). We have been unable to formulate a plausible ionic mechanism for the reaction yielding acetone which is consistent with the substituent effects described in this paper.

Substituent Effects.—The importance of structures such as II and III in the resonance description of the transition state for decomposition of IV is reflected in a ρ of -1.3 in a Hammett correlation. The sign of ρ suggests that a positive charge is, indeed, developed on sulfur on going to the transition state.

The significance of the magnitude of ρ is somewhat more difficult to assess. Several other radical reactions have been found to give Hammett correlations with values of ρ similar to that observed here.[7,17] This value, -1.3, can also be compared with the value, -1.67, applicable in the solvolyses of aryl β-chloroethyl sulfides in 55% aqueous acetone at 50°.[18,19] These solvolyses proceed with a rate-determining ionization, through transition state IX, to yield cyclic sulfonium salts.



IX

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[15] A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3408, 3412 (1951).

[16] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946); W. E. Cass, *ibid.*, **68**, 1976 (1946).

[17] For a review see G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

[18] G. Baddely and G. M. Bennett, *J. Chem. Soc.*, 261 (1933).

[19] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

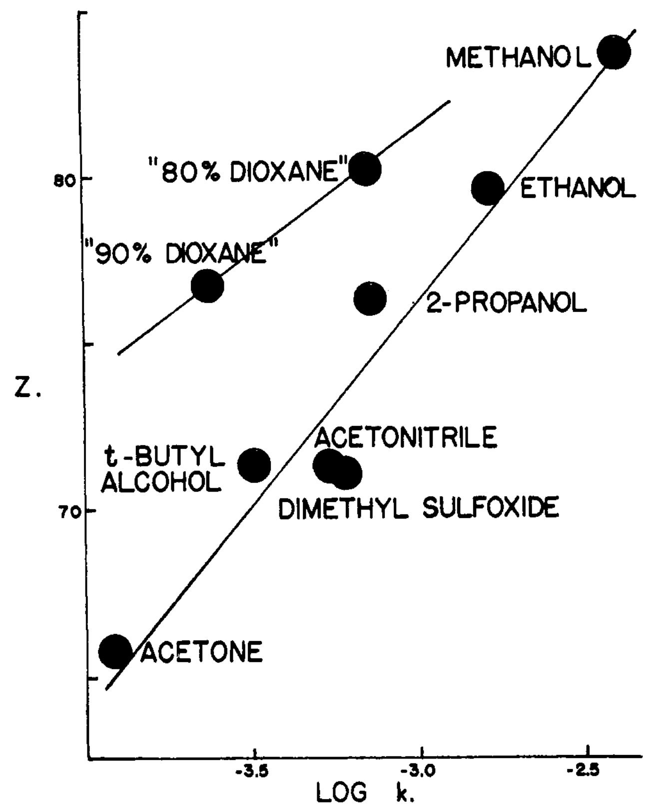

Fig. 1.—Decomposition of *t*-butyl *o*-phenylthioperbenzoate at 40° (followed by infrared spectroscopy).

Substituent effects in the two types of sulfur participation are not, however, completely analogous. Whereas *t*-butyl *o*-phenylthioperbenzoate decomposes more rapidly than its *o*-methylthio analog,[1] the substitution of methyl for phenyl in the chlorosulfide precursor to IX has the opposite effect of increasing the rate of ionization.[20] This possibly reflects a certain amount of radical character in the transition state for the perester decomposition, making possible a type of resonance interaction with the phenyl ring which is not possible in the mustard analog.

Many free-radical reactions involving the development of a positive charge on a benzyl carbon atom in the transition state have been shown[7,17] to give better correlation with σ^+-constants[21] than with σ-constants. It is interesting that in the perester decomposition reported here there is a much better correlation with σ than with σ^+. Apparently the increased electron demand accompanying the formation of a sulfonium-like sulfur atom is not sufficient to bring about an important resonance interaction with a *p*-methoxyl group.[22] A replot of the data of Baddely and Bennett[18] shows a much better correlation with σ than with σ^+ in this closely analogous ionization of a β-chlorosulfide.

The Effect of Solvent Polarity.—A cursory glance at Table I reveals the large influence of solvent on rate. If an appreciable contribution to the transition state for the decomposition of this perester is made by dipolar structures such as II or III, the dependence upon solvent may be one involving solvent ionizing power, a polar solvent effect. Accordingly, the data for the decomposition have been examined in terms of three independent measures of solvent polarity.

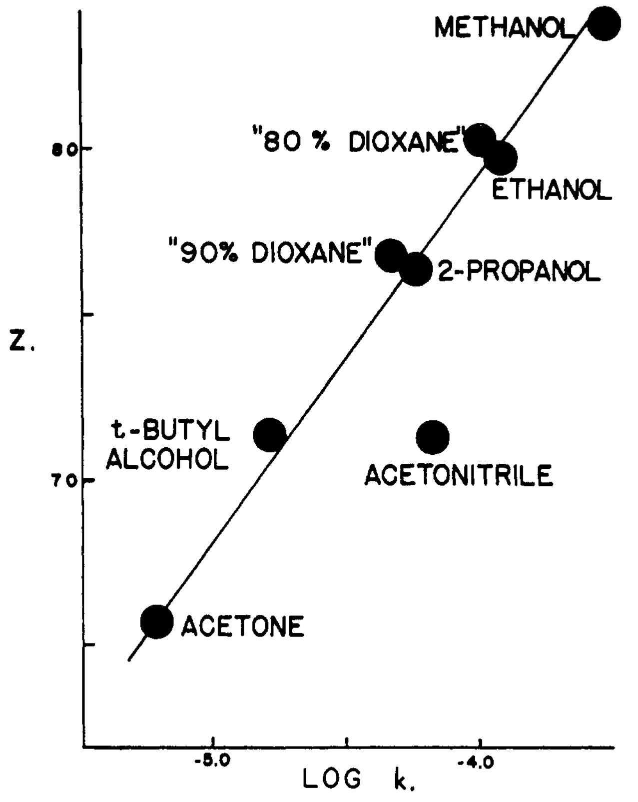

Fig. 2.—Decomposition of *t*-butyl *o*-phenylthioperbenzoate at 25° as measured by radical scavenging.

The lack of correlation between our rate data and the dielectric constant of the medium is not surprising. It has been emphasized repeatedly[23] that the dielectric constant, a measure of a macroscopic property of the medium, does not serve as a measure of the ionizing power of the solvent.

The *Z*-values of Kosower,[24] based on charge transfer spectra of pyridinium iodides, may be used to extend established scales of solvent polarity[25,26] to solvents of lesser polarity, such as those found suitable for these studies. The dispersion into two distinct lines (Fig. 1) is not surprising,[27] since specific interactions with solvents would be expected to be quite different in these reactions and in the electronic transitions upon which the *Z*-scale is based.

The log *k* obtained by galvinoxyl scavenging at 25° is plotted *vs.* *Z* in Fig. 2. The effect of solvent polarity is seen to be similar in most respects to that observed in Fig. 1. The separate line observed in Fig. 1 for aqueous dioxane mixtures is absent in Fig. 2, a result of the extremely efficient scavenging of radical fragments by galvinoxyl in aqueous dioxane mixtures.

The scale of solvent ionizing power of Smith, Fainberg and Winstein,[23] based on the ionization of *p*-methoxyneophyl *p*-toluenesulfonate, gives a very good correlation with our data[11] (Fig. 3), indicating for our perester decomposition a sensitivity to solvent polarity about 64% of that observed in the ionization of the tosylate.

The marked response of this reaction to changes in solvent polarity is to be contrasted with the insensitivity of many of the other radical reactions which give evidence for dipolar transition states through substituent effect studies. Bartlett and Rüchardt,[7] for example,

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[20] E. A. Braude and O. H. Wheeler, *J. Chem. Soc.*, 329 (1955).

[21] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957); D. E. Pearson, J. F. Baxter and J. C. Martin, *ibid.*, **17**, 1511 (1952).

[22] See H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959), for a discussion of this point. Also see F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **78**, 87 (1956), and **79**, 717 (1957), for evidence that such resonance may be important in another system.

[23] S. G. Smith, A. H. Fainberg and S. Winstein, *ibid.*, **83**, 618 (1961).

[24] E. M. Kosower, *ibid.*, **80**, 3253, 3261 (1958).

[25] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

[26] S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

[27] A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1597, 1602, 1608 (1957).

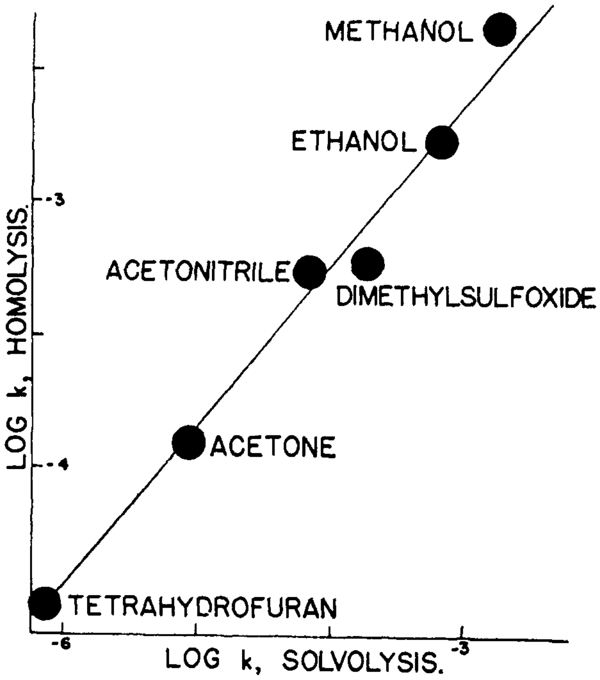


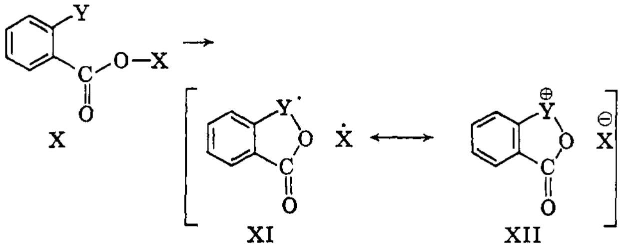
Fig. 3.—Rate of decomposition of *t*-butyl *o*-phenylthioperbenzoate at 40° *vs.* rate of solvolysis of *p*-methoxyneophyl *p*-toluenesulfonate.

report that a *t*-butyl phenylperacetate decomposition, characterized by a ρ of -1.09, is faster in ethanol than it is in cyclohexane by a factor of only 3.8, at 70°. Such a change in solvents for the reaction reported in this paper produces a change in rate nearly 100 times greater than this.

Salt Effects.—The operation of a salt effect in a reaction in which 88–93% of the radicals which can theoretically be produced are scavenged by galvinoxyl demonstrate convincingly that polar contributions are important to a description of the transition state. The correlation between the solvent effect in the decomposition of the perester and the effect for the solvolysis of *p*-methoxyneophyl tosylate (Fig. 3) indicate that the radical reaction is not as sensitive to solvent-ionizing power as is the solvolysis. Similarly, the effect of added salt is not as striking for the homolysis as it is for the ionization. The constant b in eq. 1,[28] describing the effect of added lithium perchlorate, is 76; the value of b for the same salt is the solvolysis of the tosylate in tetrahydrofuran has been evaluated[29] as 482.

$$k = k_0(1 + b[\text{salt}]) \qquad (1)$$

Dependence on Leaving Group.—If neighboring group participation in free radical reactions of the type discussed here can be discussed generally in terms of a transition state described by canonical forms XI and XII, analogous to I and II, it is clear that the rate should depend not only on Y but also on the nature of the leaving group, X.



X XI XII

In the cases where neighboring iodine participation has been observed (–Y = –I) three different leaving groups, –X, have been studied.[1,9] To the extent that the dipolar structure XII is important in the description of the transition states for these reactions we may predict that the rates of the reactions should be correlated with the ability of X to act as an anionic leaving group. If the K_a for the corresponding acid HX is taken as a measure of this ability, we can see from Table VI that a semiquantitative correlation exists.

Table VI

Decomposition of X (Y = I)

–X	Rel. rate of decompn.	K_A for HX[a]
o-Iodobenzoate[9]	10^4	1.37×10^{-3}
p-Nitrobenzoate[9]	10^3	3.76×10^{-4}
t-Butoxy[1]	1	Small

[a] Values listed by J. F. J. Dippy, *Chem. Rev.*, **25**, 151 (1939).

This is consistent with the idea that the polarization of the transition state for the decomposition of *t*-butyl *o*-iodoperbenzoate (X, Y = I; X = *t*-butoxy) is such as to place a positive charge on iodine. This is, therefore, in the same sense as in the sulfur-containing perester where substituent effects indicate clearly the development of a positive charge on sulfur and, to the extent that the two systems are parallel, points to the importance of II in the description of the transition state in the decomposition of IV.

Steric Effects.—Substitution of an *o*-methylsulfonyl group into *t*-butyl perbenzoate elicits the slight retardation in the rate of decomposition (compound V, Tables I and II) expected[4,6] for such an electron-withdrawing substituent. The absence of anchimeric assistance in the thermal decomposition of V is not surprising. An appreciable steric hindrance to the intimate approach of the sulfur atom to the alkyl oxygen of the carboxylate group is provided by the groups attached to sulfur. Sulfur participation would involve the formation of a pentacoördinate sulfur atom.

The low rates of decomposition observed for VI and VII, essentially identical with the rate for the unsubstituted perbenzoate VIII, reflect a lack of anchimeric acceleration in these close analogs of *t*-butyl *o*-phenylthioperbenzoate (IV, X = H). These model compounds differ from IV with respect to geometric restrictions and to electronic effects of possible importance in determining the energy of the transition state for decomposition.

We must consider the possibility that the slow decomposition of VII reflects the electronic effects of the electron-withdrawing carbonyl substituent, which retard the rate of decomposition to the point at which anchimeric acceleration is unimportant. The substituent effects may be estimated if one assumes that ρ is identical for substituents on either ring and that the same substituent constant, σ, may be used for an *o*-benzoyl group as for a *p*-benzoyl substituent. It is found that the rate so calculated is faster than the experimental rate constant for the decomposition of VII by a factor of more than 10^3 at 50°. Clearly the observed absence of rate enhancement is not accounted for by an electronic effect of the thioxanthone carbonyl.

The other model compound VI, in which the neighboring sulfur atom is a part of a heteroaromatic ring system, differs electronically from IV in a manner more difficult to evaluate.

Compounds VI and VII exhibit a common structural feature in the inclusion of the neighboring sulfur atom in a ring system. This suggests the possibility that

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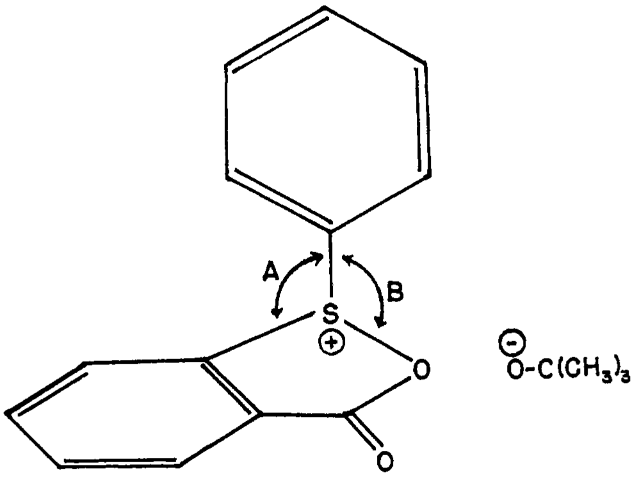
[28] S. Winstein, E. Clippinger and A. H. Fainberg, *J. Am. Chem. Soc.*, **76**, 2597 (1954).

[29] S. Winstein, S. Smith, D. Darwish and G. C. Robinson, *ibid.*, **81**, 5511 (1959).

bridged transition states are precluded in these systems by a geometrical factor.

It is conceivable that this geometrical factor is simply an internuclear distance which is too great to accommodate S–O bond formation in the transition state. The S–O internuclear distances in the hypothetical transition states for the decompositions of VI, VII and IV have been approximated by simple trigonometric calculations, using bond lengths and angles based on those of suitable models. They are found to vary by a maximum of 0.07 Å., assuming unstrained models for the three transition states. This makes it seem unlikely that the failure of VI and VII to give evidences of anchimeric acceleration is the result of an excessive S–O internuclear distance in these peresters.

The dibenzothiophene ring system is planar. The angle between the planes of the aromatic rings in thioxanthone is about 146° (estimated from Büchi molecular models). In the decomposition of either VI or VII through a bridged transition state, the S–O bond must certainly be nearly coplanar with the two C–S bonds. The only significant difference in geometry between *t*-butyl *o*-phenylthioperbenzoate (IV) and the other two systems is the difference in the freedom of rotation around the C–S bond. It is concluded, therefore, that anchimeric acceleration by sulfide sulfur in the decomposition of peresters of the type studied is possible only when the bonds to sulfur may assume a relationship which differs appreciably from coplanarity.



The similarity between the non-planar geometry of the transition state proposed for this decomposition and the geometry of sulfonium ions suggests the importance of canonical form II in a description of this transition state.[12] The more explicit representation, XIII, recognizes the geometric requirement for the reaction, with both angle A and angle B being considerably less than 120°.

The possible importance of canonical form III in the description of the transition state for the decomposition of IV was mentioned in an earlier publication.[11] The structure is reminiscent of a radical ion product proposed by Walling[30] in a mechanistic interpretation of the radical portion of the reaction between benzoyl peroxide and dimethylaniline.

Evidence for this type of interaction might be sought in the rate of the thermal decomposition of *t*-butyl *p*-methylthioperbenzoate. No acceleration comparable to that observed[11] for the *ortho* isomer was observed. The electrostatic effect associated with the greater charge separation in the *para* isomer would be expected to be too small to explain the observed differences in reactivity.

The lack of anchimeric assistance in the decomposition of peresters VI and VII implies a restriction of rotation about the C–S bond in the transition state for decomposition of IV. The most straightforward interpretation of these results invokes the formation of an S–O bond in the transition state, involving essentially sp^3-hybridization of the sulfur electrons. Structure III provides no basis for an understanding of the geometric restrictions on the transition state for the decomposition of IV for which this study has provided evidence.

The total evidence suggests that the transition state for the decomposition of IV is best described by canonical form II with much lesser contributions of undetermined importance from I and III.

Experimental[31]

Materials.—Chlorobenzene, cyclohexane, pyridine and *t*-butyl hydroperoxide were purified as previously described.[1] Acetone, acetonitrile and dimethyl sulfoxide were purified by the method of Smith, Fainberg and Winstein.[23] Dioxane, nitrobenzene, tetrahydrofuran and 2-propanol were purified according to Fieser.[32] *t*-Butyl alcohol was purified by the procedure of Kosower.[24] Reagent grade ethanol, methanol and ether were used without further purification. Lithium perchlorate was dried over phosphorus pentoxide at 110° in an Abderhalden drying apparatus.

***t*-Butyl *o*-Phenylthioperbenzoate.**—Anthranilic acid was converted to *o*-phenylthiobenzoic acid.[33] The acid was converted to an 80% yield of the acid chloride by treatment with excess thionyl chloride. The method of Martin and Bentrude[1] yielded *t*-butyl *o*-phenylthioperbenzoate in 28% yield, m.p. 60–61°.

***t*-Butyl *o*-(*p*-Anisylthio)-perbenzoate.**—Sodium (1.4 g., 0.061 g.—atom) was treated with 120 ml. of methanol. This solution was cooled to 0° and a solution of methyl thiosalicylate[34] (10 g., 0.061 mole) in 120 ml. of methanol was added. The cold solution was stirred and swept with nitrogen. A solution of 4,4′-dimethoxydiphenyliodonium trifluoroacetate[35] (8.5 g., 0.0185 mole) in methanol was added in small portions over a period of several minutes. After 1-hour reflux, the mixture was cooled to room temperature and filtered. Further cooling of the filtrate caused the precipitation of 14 g. of impure methyl *o*-(*p*-anisylthio)-benzoate, m.p. 78–81°. The impure ester was saponified with alcoholic potassium hydroxide and extracted with ether. Acidification of the aqueous layer gave the crude acid, a white solid, in 44% yield (7.0 g., 0.027 mole), m.p. 224–228° (lit.[36] 232°). A portion was recrystallized from methanol to analytical purity, m.p. 232°.

Anal. Calcd. for $C_{14}H_{12}O_3S$: C, 64.59; H, 4.65. Found: C, 64.29; H, 4.75.

The *o*-(*p*-anisylthio)-benzoic acid was converted to the acid chloride by a 12-hr. treatment with excess thionyl chloride and recrystallized from ether to give a yellow solid, m.p. 91–92°, yield 62%.

Anal. Calcd. for $C_{14}H_{11}ClO_2S$: C, 60.32; H, 3.97. Found: C, 58.48; H, 3.82.

The perester was synthesized in a 12% yield by the usual procedure[1]; m.p. 55–56°.

Anal. Calcd. for $C_{18}H_{20}O_4S$: C, 65.04; H, 6.07. Found: C, 64.72; H, 6.38.

***t*-Butyl *o*-(*p*-Chlorophenylthio)-perbenzoate.**—The synthesis of *o*-(*p*-chlorophenylthio)-benzoic acid was carried out by a procedure similar to that for the preparation of *o*-(*p*-anisylthio)-benzoic acid. The addition of a slurry of 4,4′-dichlorodiphenyliodonium bromide in methanol to a stirred solution of the sodium salt of methyl thiosalicylate under nitrogen, followed by saponification of the ester produced a 40% yield of the acid, m.p. 236–237°.

Anal. Calcd. for $C_{13}H_9ClO_2S$: C, 58.97; H, 3.43. Found: C, 59.08; H, 3.49.

Treatment of this acid with excess thionyl chloride converted it to the acid chloride, a white solid, which was recrystallized from ether–pentane; yield 68%, m.p. 88–88.5°.

Anal. Calcd. for $C_{13}H_8Cl_2O_2S$: C, 55.12; H, 2.85. Found: C, 55.35; H, 3.04.

The perester was routinely synthesized in 39% yield by the usual procedure; m.p. 69–69.5°.

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(30) C. Walling and N. Indictor, *J. Am. Chem. Soc.*, **80**, 5814 (1958).

(31) All melting points are corrected.

(32) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957.

(33) W. S. Weedon and H. W. Doughty, *Am. Chem. J.*, **33**, 386 (1950).

(34) L. Gattermann, *Ber.*, **32**, 1150 (1899).

(35) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner and E. Sommer, *J. Am. Chem. Soc.*, **81**, 342 (1959).

(36) K. C. Roberts and S. Smiles, *J. Chem. Soc.*, 863 (1929).

Anal. Calcd. for $C_{22}H_{17}ClO_3S$: C, 60.64; H, 5.02. Found: C, 60.65; H, 4.96.

t-Butyl o-(p-Nitrophenylthio)-perbenzoate.—o-(p-Nitrophenylthio)-benzoic acid was prepared in a 22% yield by the procedure of Mann and Turnbull[37]; m.p. 226–227° (lit.[37] 227–228°). This acid (10 g., 0.036 mole) was refluxed with excess thionyl chloride for several hours. Removal of the thionyl chloride by distillation left impure acid chloride, which was recrystallized from ether–pentane; 8.0 g. (0.027 mole, 75%), m.p. 131–132°. Treatment of this acid chloride with t-butyl hydroperoxide in the presence of pyridine in the usual manner prepared the perester in 46% yield, m.p. 84–84.5°.

Anal. Calcd. for $C_{17}H_{17}NO_5S$: C, 58.77; H, 4.93. Found: C, 59.00; H, 4.87.

Galvinoxyl.—The radical scavenger, galvinoxyl, was synthesized by the method of Kharasch and Joshi[38]; m.p. 154–155° (lit.[38] 157°).

Decomposition of t-Butyl o-Phenylthioperbenzoate in Acetic Acid.—The perester (0.13 g., 0.00043 mole) in 4 ml. of acetic acid in a sealed tube was heated on a steam-bath for 2 hours. The tube was opened, a small amount of ethanol was added and the volatile materials were distilled. The addition of 2,4-dinitrophenylhydrazine reagent caused the precipitation of the dinitrophenylhydrazone of acetone; yield 15% (16 mg., 0.000067 mole), m.p. 124–125° (lit.[39] 126°).

t-Butyl o-Methylsulfonylperbenzoate (V).—Technical grade o-mercaptobenzoic acid was methylated with alkaline dimethyl sulfate according to the procedure of Friedlaender,[40] and the methylated acid was oxidized to o-methylsulfonylbenzoic acid by the method of Arndt, Kirsch and Nachtwey.[41] Treatment of this acid with thionyl chloride yielded the acid chloride (88%), m.p. 59–60°.

Anal. Calcd. for $C_8H_7O_3ClS$: C, 43.94; H, 3.21. Found: C, 44.20; H, 3.48.

A solution of the acid chloride (4.0 g., 0.018 mole) in 75 ml. of ether was added slowly to a solution of t-butyl hydroperoxide (2.55 g., 0.028 mole) and pyridine (1.6 g., 0.020 mole) in 100 ml. of ether.

The mixture was allowed to stir overnight, then was filtered to remove pyridinium hydrochloride. Chromatography through basic alumina, eluting with ether, removed t-butyl hydroperoxide. Recrystallization from ether–pentane yielded the perester, 1.06 g. (0.003 mole, 17%), m.p. 74–75°.

Anal. Calcd. for $C_{12}H_{16}O_5S$: C, 52.94; H, 5.88. Found: C, 52.89; H, 6.03.

t-Butyl Dibenzothiophene-4-percarboxylate (VI).—A solution of dibenzothiophene-4-carboxylic acid chloride[42,43] (3.72 g., 0.015 mole) in 500 ml. of methylene chloride was added slowly to a stirred solution of pyridine (2.0 g., 0.0253 mole) and t-butyl hydroperoxide (1.7 g., 0.0189 mole) in 75 ml. of methylene chloride at 0°. The mixture was stirred at 0° for 6 days, then filtered to remove pyridinium chloride and chromatographed through basic alumina, eluting with ether. The crude perester was recrystallized from ether–pentane to give 0.67 g. (0.0023 mole, 15%) of VI, m.p. 79–80°.

Anal. Calcd. for $C_{17}H_{16}O_3S$: C, 68.00; H, 5.33. Found: C, 67.66; H, 5.36.

t-Butyl Thioxanthone-4-percarboxylate (VII).—Treatment of thioxanthone-4-carboxylic acid[44,45] with excess thionyl chloride produced the acid chloride in 69%, m.p. 202–204°. Perester VII was prepared in a 14% yield from this acid chloride in a manner analogous to the preparation of VI; m.p. 132–133° dec.

Anal. Calcd. for $C_{18}H_{16}O_4S$: C, 65.83; H, 4.91. Found: C, 65.55; H, 4.83.

Kinetic Analysis.—A description of the technique employed may be found in part II of this series.[1]

The rate constants were determined by the method of least squares.[46]

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(37) F. G. Mann and J. H. Turnbull, *J. Chem. Soc.*, 747 (1951).

(38) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

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

(40) P. Friedlaender, *Ann.*, **351**, 390 (1907).

(41) F. Arndt, A. Kirsch and P. Nachtwey, *Ber.*, **59**, 1074 (1926).

(42) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

(43) H. Gilman and S. Avakian, *J. Am. Chem. Soc.*, **68**, 2104 (1946).

(44) H. Gilman and D. L. Esmay, *ibid.*, **75**, 278 (1953).

(45) F. Mayer, *Ber.*, **43**, 584 (1910).

(46) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

The Decomposition of Certain 1,1-Disubstituted 2-Arenesulfonylhydrazine Salts

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The behavior in ether solvents at elevated temperatures of N-benzenesulfonamidopyrrolidine, N-tosylamidopyrrole and N-benzenesulfonamidocarbazole sodium salts has been studied. Mechanisms are proposed for the observed decompositions and inferences are drawn regarding the chemistry of diazenes (aminonitrenes).

Introduction

Oxidation of 1,1-disubstituted hydrazines generally leads to tetrazenes, often in quantitative yields. Certain 1,1-dialkylhydrazines undergo fragmentation when oxidized, however, yielding nitrogen and the products of disproportionation and/or coupling of the alkyl groups. This so-called "abnormal" reaction has been observed only where one[2] or both[3,4] of the α-carbons bears a substituent capable of stabilizing charge or radical character (*e.g.*, aryl or cyano) in the transition state for decomposition. Fragmentation also occurs in sodium hydrosulfite reductions of nitrosamines (which normally give hydrazines), but only if these special substituents are present.[4,5] Carpino discovered that the base-catalyzed decomposition of

$$2R_2NNH_2 \xrightarrow{[O]} R_2N{-}N{=}N{-}NR_2$$

$$\left.\begin{array}{l} R_2'NNH_2 \xrightarrow[-N_2]{[O]} \\ \\ R_2'NNO \xrightarrow[\substack{NaOH \\ -N_2}]{Na_2S_2O_4} \end{array}\right\} R'_{-H},\ R'_{+H} \text{ and/or } R'{-}R'$$

1,1-dibenzyl-2-benzenesulfonylhydrazine gave nitrogen and bibenzyl in high yield,[6] and fragmentation in an analogous fashion has been shown to occur with a

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[1] Monsanto Summer Research Fellow, 1961; du Pont Summer Research Fellow, 1962.

(2) C. G. Overberger and L. P. Herin, *J. Org. Chem.*, **27**, 417 (1962); L. A. Carpino, A. A. Santilli and R. W. Murray, *J. Am. Chem. Soc.*, **82**, 2728 (1960).

(3) C. G. Overberger, *Rec. Chem. Progr.*, **21**, 21 (1960).

(4) See for example, C. G. Overberger, N. P. Marullo and R. G. Hiskey, *J. Am. Chem. Soc.*, **83**, 1374 (1961); C. G. Overberger and L. P. Herin, *J. Org. Chem.*, **27**, 2423 (1962).

(5) C. G. Overberger and N. P. Marullo, *J. Am. Chem. Soc.*, **83**, 1378 (1961).

(6) L. A. Carpino, *ibid.*, **79**, 4427 (1957).