at 186–187° at 0.15 mm., was obtained in 55% yield. Analysis is reported in Table V.

Rate Measurements.—The piperidine used as solvent and catalyst for hydrolysis of the triarylsilanes was an Eastman Kodak Co. white label product which had been redistilled through a twelve-inch column packed with 1/8 inch glass helices. Distilled water was added to this material until the water concentration was 0.96 molar, as determined by titration with the Karl Fischer reagent. The silanes were redistilled at reduced pressure from a flask having a five-inch Vigreux neck until a sample was obtained which, when hydrolyzed, would give a total volume of hydrogen equal to 100.0 ± 0.3% of the theoretical volume. In most cases not more than two distillations were required.

The kinetic runs were made as follows. Depending upon the size of the sample to be used, either 10 or 20 ml. of the piperidine reagent described above was pipetted into a 50-ml. erlenmeyer flask, which was placed in the clamp of a shaking machine arranged in such a way that about half the height of the flask was immersed in an oil-bath maintained at 38.80 ± 0.05°. The flask was loosely stoppered, the shaker started, and the contents allowed 15 minutes to come to bath temperature. The sample (0.1–0.4 g.) was weighed into a small glass cup made by cutting the bottom from a 12 cm. test-tube just above its hemispherical base. The shaker was stopped, cup and sample were dropped into the erlenmeyer flask, and the flask was connected to a 10-ml. gas buret by means of capillary glass tubing and a short length of Tygon tubing. Shaker and timer were then started, and the volume of hydrogen was read at intervals. No advantage was found in the use of a flask with side bulb to hold the piperidine so that the system could be closed before silane and base were mixed, since there was no evolution of hydrogen during the few moments between mixing the reagents and starting the shaker. A constant positive blank of 0.10 ml. of hydrogen was observed for all runs.

Analysis of the silanes for hydrogen as Si–H was carried out in the same way, except that a few pellets of potassium hydroxide were added to the piperidine in order to hasten the reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CARSON–NEWMAN COLLEGE]

Quaternary Salts of Styryl Pyridines and Quinolines

BY CARL T. BAHNER, EDWIN S. PACE AND ROBERT PREVOST

New quaternary salts of substituted styryl pyridines and quinolines have been prepared for cancer chemotherapy screening and their physical properties have been described.

Continuing the search for additional compounds which are capable of damaging malignant cells *in vivo*,[1] quaternary salts of styryl substituted pyridines and quinolines have been prepared. These series were selected for study because a number of the compounds known to have anti-tumor action are quaternary salts which contain two rings joined by a two carbon chain,[2] 4-dimethylaminostilbene

TABLE I

QUATERNARY SALTS OF STYRYL PYRIDINES AND QUINOLINES

Methiodide salt of	Empirical formula	M.p., °C.	Analyses, % Calcd.	Found[a]
2-(*p*-Dimethylaminostyryl)-quinoline	$C_{20}H_{21}IN_2$	276	I, 30.49	30.46
2-(*p*-Diethylaminostyryl)-quinoline	$C_{22}H_{25}IN_2$	224–226	I, 28.56	28.42
2-(2,4-Dichlorostyryl)-quinoline	$C_{18}H_{14}Cl_2IN$	226–227	I, 28.71	28.40
2-(2,6-Dichlorostyryl)-quinoline	$C_{18}H_{14}Cl_2IN$	247–248	I, 28.71	28.82
4-(*o*-Hydroxystyryl)-quinoline	$C_{18}H_{16}INO$	272–273	C, 55.55	55.56
			H, 4.14	4.22
2-(3,4-Dichlorostyryl)-quinoline	$C_{18}H_{14}Cl_2IN$	255–256	I, 28.71	28.62
2-(*p*-Methoxystyryl)-quinoline	$C_{19}H_{18}INO$	236–237	I, 31.47	31.43
2-(*o*-Ethoxystyryl)-quinoline	$C_{20}H_{20}INO$	224–226	I, 30.42	30.47
2-(2,3-Dimethoxystyryl)-quinoline	$C_{20}H_{20}INO_2$	224–225	I, 29.29	29.27
2-(3,4-Dimethoxystyryl)-quinoline	$C_{20}H_{20}INO_2$	259–260	C, 55.44	55.56[b]
			H, 4.65	4.46
2-(3,4-Diethoxystyryl)-quinoline	$C_{22}H_{24}INO_2$	239–240	C, 57.28	57.22[c]
			H, 5.24	5.33
2-(3,4-Methylenedioxystyryl)-quinoline	$C_{19}H_{16}INO_2$	259–260	I, 30.42	30.41
6-Ethoxy-2-(*p*-dimethylaminostyryl)-quinoline[d]	$C_{22}H_{25}IN_2O$	274–276	C, 57.39	57.07[b]
			H, 5.47	5.55
4-(*p*-Dimethylaminostyryl)-quinoline	$C_{20}H_{21}IN_2$	302	I, 30.49	30.35
4-(*p*-Diethylaminostyryl)-quinoline	$C_{22}H_{25}IN_2$	273–275	I, 28.56	28.40
2-(*o*-Ethoxystyryl)-pyridine	$C_{15}H_{18}INO$	252–253	I, 34.56	34.49
2-(3,4-Diethoxystyryl)-pyridine	$C_{18}H_{22}INO_2$	231–232	I, 30.88	30.73
2-(*p*-Nitrostyryl)-pyridine	$C_{14}H_{13}IN_2O_2$	262–263	I, 34.47	34.51
Allyl bromide salt of				
2-Styrylquinoline	$C_{20}H_{18}NBr$	234–235	Br, 22.69	22.68

[a] Average of two Volhard analyses for ionic halogen unless otherwise indicated. [b] Carbon and hydrogen analyses by Galbraith Microanalytical Laboratories. [c] Carbon and hydrogen analyses by Analytical Laboratory of National Cancer Institute. [d] *Cf.* Browning, *et al.*, ref. 4.

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and 2-dimethylaminostilbene have been reported to inhibit growth of Walker carcinoma of the rat,[3] and several styryl compounds have been reported to be germicides[4] or to inhibit aerobic glycolysis.[5] The method of Phillips[6] was employed in preparing the compounds listed.

The *p*-dialkylaminostyrylquinolinium salts were deep purple or green crystalline solids which formed purple solutions in water, while the other salts ranged from yellow to red in color and formed yellow or orange solutions. The solubilities in hot water were of the order of 0.01–0.5%. In most instances the color was destroyed or weakened by dilute nitric acid so that determination of the ionic halogen content by Volhard analyses was satisfactory.

Samples have been submitted to interested groups for screening against tumors in mice and for testing as plant growth control substances.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Kinetics of the Thermal Decomposition of Peresters. I. The Effect of Perbenzoate Concentration on the Decomposition of *t*-Butyl Perbenzoate[1]

BY A. T. BLOMQUIST AND ARTHUR F. FERRIS[2]

The thermal decomposition of *t*-butyl perbenzoate has been studied at several different temperatures and initial peroxide concentrations in *p*-chlorotoluene and at two concentrations at one temperature in chlorobenzene and xylene. The increase in the over-all first order rate constant with increasing initial peroxide concentration is small but real and appears to be caused by free radical attack on undecomposed peroxide, since it was eliminated by acetanilide, a known free radical inhibitor. The method developed by Nozaki and Bartlett for calculating unimolecular rate constants did not give consistent results when applied to perbenzoate data. The energy of activation for the decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene was calculated to be 34.5 kcal./mole.

It has been shown recently that the rate of the thermal decomposition of benzoyl peroxide increases with increasing initial peroxide concentration in a given solvent[3] and varies widely from solvent to solvent.[4] It appears clear that the unimolecular cleavage of the peroxide is accompanied by a higher order reaction, and considerable evidence has been accumulated to indicate that this is a radical induced attack on undecomposed peroxide.[4a,5b] On the other hand, the decomposition of di-*t*-butyl peroxide appears to be a simple unimolecular reaction, proceeding at essentially the same rate in the vapor phase and in widely different solvents, and showing no concentration effect.[6]

In view of the detailed study which has been made of the kinetics of the decomposition of benzoyl peroxide and di-*t*-butyl peroxide it is somewhat surprising that only fragmentary reports have been published[7] on the kinetics of the decomposition of *t*-butyl perbenzoate, which is, in a sense, intermediate between them. This paper presents the results of a study of the effect of initial peroxide concentration on the rate of decomposition of *t*-butyl perbenzoate. The effect of solvent and the effect of strong acid are discussed in a following paper.

Experimental

The decomposition of the perbenzoate was followed by periodically withdrawing samples of reaction mixtures and analyzing them for undecomposed perbenzoate iodometrically.

***t*-Butyl Perbenzoate.**—The *t*-butyl perbenzoate used in the first part of this investigation was prepared by the method of Milas and Surgenor.[8] Distillation from a cold finger type of molecular still at about 70° (0.05 mm.) gave a product which typically showed the following properties: $n^{20}D$ 1.4990, d^{20}_4 1.0427, % active oxygen 8.13 (theoretical 8.24%, hence purity 98.7%). Later in the investigation undistilled perbenzoate freed of low boiling impurities by prolonged vacuum treatment and having a purity of 95.5% was used, and still later commercial perbenzoate from the Lucidol Division of the Novadel-Agene Corporation Buffalo, New York, likewise freed from low boiling impurities and showing a purity of 96.3%. Both of the later samples decomposed at essentially the same rate as the highly purified material in *p*-chlorotoluene under standard test conditions (temperature 119.4°, peroxide concentration 0.065 *M*).

***p*-Chlorotoluene.**—Most of the *p*-chlorotoluene used in this investigation was prepared in the student laboratory of

(1) Taken from the thesis of A. F. Ferris presented to the Graduate School of Cornell University in September, 1950, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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