TABLE I

2-TOLYL-1-ETHYNYLCYCLOHEXANOLS AND CORRESPONDING 3,5-DINITROBENZOATE DERIVATIVES

2-Tolyl-1-ethynyl-cyclohexanols	B.P., ° C.	Mm.	C		H	
			Calcd.	Found	Calcd.	Found
1. 2-(*o*-Tolyl)-	131–132	~2	84.07	84.11	8.47	8.38
2. 2-(*m*-Tolyl)-	115	0.45	84.07	84.02	8.47	8.48
3. 2-(*p*-Tolyl)-	134	~2	84.07	84.19	8.47	8.11

3,5-DINITROBENZOATES OF ABOVE CYCLOHEXANOLS

Derivative of:	M.P., ° C.	C		H		N	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
1. 2-(*o*-Tolyl)-	168–169	64.69	64.52	4.94	4.82	6.86	6.75
2. 2-(*m*-Tolyl)-	161.5–162.5	64.69	64.51	4.94	4.90	6.86	6.80
3. 2-(*p*-Tolyl)-	161–162	64.69	64.83	4.94	4.82	6.86	6.70

stance gave 12 g. of colorless viscous liquid, b.p. 131–132° at about 2 mm.

Under the same conditions 21 g. of 2-(*m*-tolyl)cyclohexanone gave 16.4 g. of 2-(*m*-tolyl)-1-ethynylcyclohexanol and 1.54 of unreacted ketone. With the para isomer less than one gram of unreacted ketone was recovered from 18 g. of starting ketone. All three products gave a precipitate when treated with alcoholic ammoniacal silver nitrate solution.

The methylal was treated with sodium for a few days then fractionated through a Todd precise fractionation assembly with a 90 cm. column packed with glass helices and subsequently stored over sodium wire.

3,5-Dinitrobenzoates. A mixture of 0.5 g. of the cyclohexanol, 0.52 g. of 3,5-dinitrobenzoyl chloride, and 5 ml. of pyridine was allowed to stand at room temperature for 24 hr. The mixture was then warmed on a water bath for 5 min., poured into 20 ml. of water and extracted with ether. The ether solution was washed with 1% HCl followed by 1% sodium carbonate and water.

Infrared absorption spectra. The I. R. spectra[6] of all three isomers, taken on pure liquid samples, have a sharp ≡C—H stretching absorption band at 3270 cm.$^{-1}$ and what could be a weak C≡C stretching band at 2090 cm.$^{-1}$; Wotiz *et al.*[7] have reported a frequency of 2080 cm.$^{-1}$ for the latter in 1-heptyn-3-ol. A strong band appears at 970, 973, and 974 cm.$^{-1}$ in the spectrum of the ortho, para, and meta isomer respectively, a region which falls within the range of characteristic absorption for cyclohexane derivatives.[8] With each isomer in the pure liquid state the O—H stretching absorption band has two distinct peaks of almost equal intensity, one at 3490 and the other at 3380 cm.$^{-1}$. These are attributed to unassociated and to hydrogen bonded hydroxyl groups. This is substantiated by the fact that when measured in 0.03*M* solution in carbon tetrachloride, with a 1 mm. liquid cell, a single sharp band appears at 3560 cm.$^{-1}$.

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(6) The spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer with NaCl prism.

(7) J. H. Wotiz, F. A. Miller, and R. J. Palchak, *J. Am. Chem. Soc.*, **72**, 5055 (1950).

(8) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Second Edition, John Wiley & Sons, Inc., New York, N. Y., 1958, p. 31.

An Improved Synthesis of Monoperphthalic Acid

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Other experiments[1] have shown the Böhme procedure[2] for preparing monoperphthalic acid from phthalic anhydride and hydrogen peroxide to be very sensitive to slight variations in experimental conditions. A modified procedure, requiring a 24 hour reaction time, has been devised, and a 65% yield of peracid reported.[1]

We have also encountered difficulty with the Böhme preparation and have overcome it by substituting sodium carbonate for sodium hydroxide as the basic agent. In this manner reproducible yields of 76–78% of ethereal solutions of monoperphthalic acid were secured in 0.5 hour reaction times. Essentially no decomposition of hydrogen peroxide was observed; this allowed the use of only a slight excess of that material, rather than the 100% excess employed in the earlier procedures.[1,2]

EXPERIMENTAL

Monoperphthalic acid. To a 1-l., round-bottomed flask, equipped with mechanical stirrer and thermometer, and cooled by an ice-salt bath, was added a solution of 62 g. (0.50 mole) of sodium carbonate monohydrate in 250 ml. of water. This was cooled to 5° and 70 g. (0.6 mole) of 30% hydrogen peroxide was added in one portion. When the temperature of the mixture reached 0°, there was added 75 g. (0.50 mole) of phthalic anhydride which had previously been pulverized to pass a 14-mesh sieve. After vigorous stirring at −5–0° for 30 min., all but a trace of the anhydride had dissolved. The solution was poured into a 2-l. separatory funnel, covered with 350 ml. of ether and treated with an

(1) E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955).

(2) H. Böhme, *Ber.* **70**, 379 (1937); *Org. Syntheses*, Coll. Vol. III, 619 (1955). See also G. B. Bachman and D. E. Cooper, *J. Org. Chem.*, **9**, 307 (1944).

ice-cold solution of 30 ml. of concentrated sulfuric acid in 150 ml. of water. The liberated monoperphthalic acid was extracted into the ether and removed completely from the water by 3 more 150-ml. portions of ether. The combined ether extracts were washed with a 200-ml. portion of 40% ammonium sulfate solution and dried overnight in the cold over 50 g. of anhydrous magnesium sulfate. Analyses[3] for both hydrogen peroxide and for monoperphthalic acid indicated the presence of less than 0.02 mole of the former and 0.39 mole (78% yield based on phthalic anhydride or 65% on H_2O_2 applied) of the latter.

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(3) F. P. Greenspan and D. G. MacKeller, *Anal. Chem.*, 20, 1061 (1948).

Basicity and Ionization Constants of Some Pyrazine Derivatives

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Pyrazine and the methyl derivatives of pyrazine are such weak bases that aqueous potentiometric titrations fail. However these bases are readily titrated in glacial acetic acid with perchloric acid. Under these conditions only one of the pyrazine nitrogens will be titrated. The ionization constant for the pyrazine derivatives is expressed as the classical concentration constant by Equation 1. The ratio of the protonated amine to free amine in aqueous solutions was determined spectrophotometrically.

$$K = \frac{[R_3NH^+]\,[OH^-]}{[R_3N]} \qquad (1)$$

where

$[R_3NH^+]$ is the molar concentration of the protonated amine ion,
$[OH^-]$ is the molar concentration of the hydroxide ion,
$[R_3N]$ is the molar concentration of the free amine.

The spectrum of 0.0002 mole of 2,5-dimethylpyrazine in a liter of tenth molar sodium hydroxide shows a broad unsymmetrical absorption peak in the region of 300 to 250 millimicrons, with an adsorption maximum at 275 millimicrons. The spectrum obtained when 0.0002 mole of the amine is dissolved in a liter of one molar hydrochloric acid shows a symmetrical peak for the same region, with an absorption maximum at 284 millimicrons. If 0.0002 mole of the amine is dissolved in a liter of tenth normal perchloric acid where glacial acetic acid is the solvent the spectrum corresponds to that obtained for the amine in the one molar hydrochloric acid. Therefore in one molar hydrochloric acid the amine is monoprotonated. When the amine is dissolved in more dilute hydrochloric acid solutions, the spectra obtained are intermediate between the two extremes. In tenth molar sodium hydroxide the spectrum is characteristic of the unprotonated amine. Using the appropriate spectra, the molar absorbancy index for the free amine and for the protonated amine can be calculated. The *p*H of the aqueous solution can be measured using the glass electrode, calibrated with reference buffers. From the *p*H, and the ionic strength, $[OH^-]$ can be estimated using the activity coefficients of Kortüm and Bockris[1] to obtain $[OH^-]$ in units of moles per liter. These measured quantities are sufficient to calculate from Equation I ionization constants for each derivative.

EXPERIMENTAL

Purified pyrazine derivatives were dissolved in various concentrations of hydrochloric acid, and in 0.1*M* sodium hydroxide. Spectral measurements were made using the Perkin-Elmer Spectracord 4000. These spectra were analyzed using the procedure above to calculate the constants in Table I.

TABLE I

IONIZATION CONSTANTS FOR PYRAZINE AND ITS METHYL DERIVATIVES (t = 25°C.)

No.	Compound	K	*p*K	Ionic Strength
1	Pyrazine	1.3×10^{-13}	12.9	0.001
2	2-Methylpyrazine	3.0×10^{-13}	12.5	0.001
3	2,5-Dimethylpyrazine	1.1×10^{-12}	11.9	0.001
4	2,6-Dimethylpyrazine	4.4×10^{-12}	11.5	0.001
5	2,3,5,6-Tetramethylpyrazine	6.7×10^{-12}	11.2	0.01

DISCUSSION

Pyrazine is a weak organic base, with a *p*K of 12.9. Substitution of a methyl group into the 2 position of the pyrazine ring approximately doubles the basicity. Introduction of another methyl group in the five position causes approximately a tenfold increase in basicity, but when the second methyl group is introduced into the six position the basicity is increased more than thirty-fold. Introduction of four methyl groups into all available positions on the pyrazine ring results in a fifty-fold increase in basicity. In summary, the basicity of the pyrazine nitrogen increases with the number of ring hydrogens replaced by methyl groups. For disubstitution the increase is greater if the two methyl groups are substituted on carbon atoms adjacent the same nitrogen.

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(1) G. Kortüm and J. O'M. Bockris, *Textbook of Electrochemistry*, 2nd ed., Vol. II, Elsevier Publishing Co., N. Y., 1951, p. 681.

Ionization Constants for Some Piperazine Derivatives

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A potentiometric titration method has been used to determine ionization constants for piperazine