in this process. This statement is based on the finding that a sample of randomly deuterated toluene HD/H_2 ratio of 0.00862; $C_6H_{4.967}D_{0.033}CH_3$ gave benzoic acid HD/H_2 ratio of 0.0114; $C_6H_{4.967}D_{0.033}COOH$ on oxidation under these conditions.

An analysis of the samples of benzoic acid obtained in the present study follows:

	Toluene		Toluene-α,α,α-d_3 (2.7 D)	
Time, Hr.	HD/H_2	$C_6H_{(5-n)}D_nCOOH$, n	HD/H_2	$C_6H_{(5-n)}D_nCOOH$, n
25	0.01522	.044	0.01424	.042
50	0.02837	.083	0.02684	.078
72	0.03899	.113	0.03747	.109
98	0.05078	.148	0.04843	.141

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Solubility Classification Test for the Differentiation of Strong and Weak, Water-insoluble Organic Bases

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Solubility classification tests for the differentiation of strong and weak, water-insoluble acids have long been a part of the customary procedure for identification of organic compounds; however, similar tests for the differentiation of strong and weak, water-insoluble organic bases are not described in the most recent editions of several widely adopted texts for qualitative organic analysis.[1-3] The absence of such tests probably is due to the lack of a simple suitable reaction solvent which would be capable of differentiating bases in a manner analogous to the differentiation of acids by sodium bicarbonate solution.

A reaction solvent that has been found suitable for such a differentiation of bases is a sodium acetate–acetic acid solution buffered at a *p*H of 5.5. Aliphatic amines (K_b 10^{-3} to 10^{-5}) are soluble in this solution, but aromatic amines and other weak bases (K_b about 10^{-10}) are not. Thus, by a simple extension of the solubility classification tests now commonly used, basic compounds may be separated into two classes by reference to their solubilities in this reagent, class B_1 to include those that are soluble and class B_2 those that are insoluble. A series of water-insoluble bases whose classifications have been determined on this basis are listed in Table I.

TABLE I

Solubilities* of Water-insoluble Bases in 5% HCl and NaOAc-HOAc Buffer[b]

Base	5% HCl	NaOAc–HOAc	Class
Tri-*n*-butylamine	+	+	B_1
N,*N*-dibenzylamine[c]	+	+	B_1
N-methyl-3-piperidylphenylcarbinol[d,e]	+	+	B_1
N-benzyl-4-piperidylphenylcarbinol[d]	+	+	B_1
N-methyl-3-benzyl-1,2,5,6-tetrahydropyridine[d]	+	+	B_1
Aniline	+	−	B_2
N,*N*-dimethylaniline	+	−	B_2
p-toluidine	+	−	B_2
p-anisidine	+	−	B_2
4-benzoylpyridine	+	−	B_2

* 0.2 ml. of liquids and 0.1 g. of solids in 3 ml. of solvent. [b] 2.0*M*. in NaOAc and 0.4*M*. in HOAc. [c] Insoluble salts precipitated from the reaction solvents. [d] Obtained through the courtesy of Glenn H. Warner, Teaching Fellow, Univ. of New Hampshire. [e] Although most of this material dissolved in NaOAc-HOAc buffer, a small quantity remained undissolved.

This same reaction solvent is also useful for the separation of a mixture of aromatic and aliphatic amines. In connection with a separate study where such mixtures are usually encountered,[4] a procedure utilizing sodium acetate–acetic acid buffer for the separation of α-*p*-methoxyphenylethylamine from *N*-ethyl-*p*-methoxyaniline was found to be more satisfactory than one previously employed.[5,6]

EXPERIMENTAL

Preparation of sodium acetate–acetic acid buffer. A solution of the desired *p*H (5.5) was prepared by dissolving 164 g. (2 moles) of anhydrous sodium acetate and 24 g. (0.4 mole) of acetic acid in sufficient water to make 1 liter of solution.

Solubility classification tests. The limits of solubility used were those described by Shriner, Fuson, and Curtin.[7] The tests were performed by placing 0.2 ml. of the amine (0.1 g. of solids) in 3 ml. of the appropriate reaction solvent, followed by vigorous shaking of the mixture. If the amine dissolved completely or was found to be appreciably more soluble than in water alone it was recorded as soluble.

Separation of mixtures of aliphatic and aromatic amines. A 50-ml. sample of a solution of α-*p*-tolylethylamine and *N*-ethyl-*p*-toluidine in ether, on titration by potentiometric techniques, was found to contain 0.78 m.equiv. of the former

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(7) Ref. 2, pp. 65–7.

and 0.62 m.equiv. of the latter. A second 50-ml. sample of the same solution, after extraction with three 20-ml. portions of sodium acetate–acetic acid buffer and drying with Drierite, was found to contain only *N*-ethyl-*p*-toluidine (0.57 m.equiv.) on titration by the same techniques.

A complete physical separation of a mixture of 1.40 g. (9.0 m.equiv.) of *α*-*p*-methoxyphenylethylamine and 1.03 g. (6.8 m.equiv.) of *N*-ethyl-*p*-methoxyaniline, dissolved in 225 ml. of ether, was accomplished by this method. The ether solution containing the amines was extracted with three 80-ml. portions of sodium acetate–acetic acid buffer. After drying the ether layer over anhydrous sodium carbonate, the ether was removed, and the residue was distilled to yield 0.46 g. of *N*-ethyl-*p*-methoxyaniline, b.p. 122–123° (8 mm.), $n_D^{25.5}$ 1.5503 (reported,[5] n_D^{26} 1.5494), hydrochloride m.p. 150–152°, (reported[5] 150–152°).

The sodium acetate–acetic acid extracts were combined and basified with 20 ml. of 20% sodium hydroxide solution. The resulting mixture was extracted with three 80-ml. portions of ether, and the ether extracts were combined and dried over Drierite. After removal of the ether, the residue was distilled to yield 0.98 g. of *α*-*p*-methoxyphenylethylamine, b.p. 117–118° (10 mm.), n_D^{27} 1.5282 (reported, n_D^{26} 1.5238,[5] n_D^{25} 1.5280[8]), hydrochloride m.p. 158.5–160° (reported,[5] 158–160°).

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Simple Method for Removal of Peroxides from Diethyl Ether[1]

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The formation of peroxides in stored ether constitutes an explosive hazard and a recurring introduction of impurity. To avoid peroxide formation, water and reducing agents are usually incorporated into commercial ether of all but the highest quality. In the latter cases, where the presence of reducing agent, *e.g.*, 2–4% ethanol, might be objectionable, it is expected that the ether will be freshly distilled before use; the higher boiling fraction will contain the peroxides. Because of the explosive hazard involved in too greatly concentrating peroxides, it is always necessary to leave a fairly large quantity of ether in the residue to be discarded.

A method has been found by which the peroxides may be quickly and simply removed from high quality ether samples, with no need for distillation apparatus and with only negligible loss of ether. The method presumably depends upon the slight ionization of the peroxides into hydrogen ion and the peroxidic anion. The latter, it has been found, is readily and firmly bound to the strong anion exchanging resin, Dowex 1, the Dowex being prepared in the hydroxyl form. The method has the additional advantage that, if desired, the peroxides may be eluted off into aqueous solutions.

EXPERIMENTAL

Four g. of Dowex 1 (hydroxyl form) were formed into a column in a 10 mm. (I.D.) tube, the constricted bottom being plugged with glass wool and the top overlaid with a circle of Schleicher and Schuell No. 410 filter paper. Approximately 20 ml. of ether were poured on the column. The ether was a sample of "Baker Analyzed" reagent grade anhydrous ether, with water content of 0.04% and ethanol of 0.01%, according to the label. The 5-lb. bottle had first been opened approximately 3 months previously. Although the ether was not then specifically tested for peroxides, it contained, again according to the label, <0.001% peroxide (as H_2O_2).

As the ether flowed through the column, the effluent was discarded until a simple drop evaporation test indicated that a negligible amount of water was left. The ether effluent was then collected. Both the effluent ether and the original ether were tested for peroxides by the KI test described in American Chemical Society specifications.[2] In this test, 10 ml. of ether are shaken with 1 ml. of fresh 10% KI solution. After 1 min., a yellow color indicates the presence of peroxide. Upon performing this test upon the effluent ether, no color was detectable in either the ether or the aqueous phase. A sample of the original ether, however, showed a strong yellow color in the aqueous phase and a light yellow in the ether phase.

The column was then treated with 0.1*M* KH_2PO_4–H_3PO_4, *p*H 2.1. Ten-ml. aliquots were placed on the column, and the corresponding 10-ml. effluents were collected and tested with KI. In this system, the "breakthrough" point is neatly indicated by the bleaching of the resin which occurs upon conversion of the hydroxyl form to the phosphate form. In this particular instance, the effluent including the breakthrough point gave a strong test for peroxides; the effluent samples immediately preceding and succeeding gave much weaker tests. Phosphate eluates from otherwise untreated Dowex 1 columns gave completely negative tests.

A test was also performed to investigate the possibility that peroxide accumulation in stored ether can be prevented by the inclusion of a small amount of the ion exchange resin. For this purpose, 500 ml. of C.P. ether was freed of peroxides by passing through a column of Dowex 1 (hydroxyl form). The peroxide-free ether was divided equally between two clear glass pressure bottles, which were placed side by side in the path of direct sunlight. One of the bottles contained 10 g. of Dowex 1 (hydroxyl form). At the intervals shown in Table I, the bottles were carefully opened without otherwise disturbing them, and 25-ml. aliquots were removed by rubber bulbed pipet and assayed for peroxide by the iodometric method of Reimers.[3] After the 7-day samples had been withdrawn, the bottles were temporarily closed and inverted twice, and the contents were re-sampled for peroxides. Table I indicates clearly the formation of peroxides in the stored ether, and the prevention of such accumulation by the incorporation of the anion exchanger. The somewhat irregular rate of formation of peroxides is probably due to daily variation in the amount of sunlight received; some of the included days were quite overcast.

It has been demonstrated[4–6] that H_2O_2 has some degrada-

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

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