Preparation of N, N-Diethyl- and N, N-Dimethylaniline Oxides

drogenation experiment; N-phenylmaleimide titration of one quarter of the solution indicated a 50% yield of 5 from bromo sulfone 34. The remainder of the purple solution was cooled quickly to -67° (Dry Ice-methylene chloride) and bromine (0.16 g) was added. After warming to room temperature, the usual work-up, followed by ptlc (silica; benzene-chloroform 1:1) afforded white crystals (0.179 g, 74%) of the high melting isomer of dibromo sulfone 35, mp 225-227°, identical with material prepared by the bromination of cis-1,3-dihydro-1,3-diphenylisothianaphthene 2,2-dioxide (33).

Anal. Calcd for $C_{20}H_{14}Br_2O_2S$: C, 50.20; H, 2.92; Br, 33.47. Found: C, 50.41; H, 3.08; Br, 33.19.

1,3-Dibromo-1,3-diphenylisothianaphthene 2,2-Dioxide (35). A solution of bromine (0.50 g) in carbon tetrachloride (100 ml) was added dropwise over 2 hr to a refluxing and irradiated (200-W tungsten bulb) solution of cis-sulfone 33 (0.50 g) in carbon tetrachloride (150 ml). After an additional 1 hr of refluxing and irradiation, solvent removal, chromatography on alumina (benzene), and repeated crystallization from benzene gave 0.300 g (41%) of dibromo sulfone 35, mp 225-227°, identical with the bromine addition product of purple sulfone 5 (see above). The benzene mother liquors gave a further 200 mg (27%) of crystals, mp 215-217°; this material was slightly different spectrally (ir, nmr) and appeared to be an impure stereoisomer of the 225° dibromide.

Reactions of 1,3-Dibromo-1,3-diphenylisothianaphthene 2,2-Dioxide (35). (a) With Sodium Iodide. Sodium iodide (0.4 g) in dry dimethylformamide (15 ml) was added to a solution of dibromo sulfone 35 (1.00 g) and N-phenylmaleimide (0.40 g) in dry dimethylformamide (30 ml) under nitrogen at room temperature. After 10 hr, the reddish solution was poured into water and the product was worked up in the usual manner, iodine being removed by a sodium sulfite wash. After silica chromatography (benzenechloroform 1:1), crystallization from benzene-pentane gave, as white crystals (0.325 g, 37%), triphenylnaphthalimide 39, mp 292-293°, identical (ir, mp) with material prepared (see above) from 1.3-diphenvlisobenzofuran.

(b) Pyrolysis. Dibromo sulfone 35 (0.500 g) was pyrolyzed as described for monobromo sulfone 34; the hot wire temperature was 400°. Purification by ptlc (silica, benzene) gave, after crystallization from benzene, yellow crystals (0.075 g) of 9-bromo-10-phenylanthracene (37), mp 145-147°

Anal. Calcd for C₂₀H₁₃Br: C, 72.01; H, 4.13; Br, 23.61. Found: C, 72.58; H, 4.36; Br, 23.96.

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Preparation and Basicities of Substituted N,N-Diethyl- and N,N-Dimethylaniline Oxides¹

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Twelve meta- and para-substituted N,N-dimethylanilines and eleven similar N,N-diethylanilines and the corresponding N-oxides have been prepared. pK a values of the amine oxides in water have been determined. They were very well correlated in the Hammett equation vs. σ^n , indicating that there is little or no conjugation from the ring through the nitrogen to the oxygen. The ρ values are entirely consistent with a reaction center one atom removed from the benzene ring ($\rho = 0.907$ for the dimethyl case and $\rho = 0.91$ for the diethyl case).

In contrast with heterocyclic amine oxides the chemistry of N,N- dialkylated aniline oxides has remained largely undeveloped since the original studies of Bamberger,³ with the exception of the Polonovski reaction 4^{-7} (N, N-dimethylaniline oxide plus acetic anhydride).

Amine oxides are unusual both in their physical properties and in the variety of chemical reactions they can undergo. The reactions of dialkylaniline oxides that have been observed, but for which there are no modern, published mechanistic studies, are the Cope elimination,⁸ the rearrangements observed upon treatment with nitrous^{2,9} or sulfurous acids,^{2,10,11} the deoxygenations and/or rearrangements resulting from treatment with various nonmetal oxides¹² and chlorides,¹³ and deoxygenation with alkyl halides.^{14,15} The rates of reaction of substituted N,N-dialkylaniline oxides can be used to obtain information about the mechanistic nature of these reactions. Since the kinetic behavior of N-oxides in protic solvents must involve acidbase ionization, the values of the K_a 's must be known before actual rate constants can be determined.

A continuing interest in these compounds, their reactions, and the mechanics of their reactions led to the syntheses and pK_a studies of N.N-dimethylaniline oxides (3) and N,N- diethylaniline oxides (4) described here.

Table I Synthesis of N,N-Dimethylanilines with Dimethyl Sulfate

Compd Yield,		Bp or Mp, °C	Bp or Mp, °C		
1c (<i>m</i> -OCH ₃)	76	66–68 (0.1 mm)	204-205 (740 mm) ⁴		
1k (<i>m</i> -Br)	81	74-76 (0.3 mm)	$100-104 (2.0 \text{ mm})^{2}$		
1g(m-F)	48	72-73 (6.0 mm)	82 (15 mm)°		
1i (<i>m</i> -C1)	43	124 (9.3 mm)	$232 (760 \text{ mm})^d$		
1f $(p-F)$	71	24	25 ^e		
$1b(p-OCH_3)$	68	47.5-48	47°		

^a Reference 27. ^b E. Schmidt and R. Schumacher, Chem. Ber., 54, 1414 (1921). ^c H. P. Crocker and B. Jones, J. Chem. Soc., 1808 (1959). ^d H. Goldschmidt and H. Keller, Chem. Ber., 35, 3542 (1902). ^e G. Schiemann and W. Winkelmuller, Chem. Ber., 36, 731 (1933).



Results

The commercially unavailable tertiary amines were prepared from the appropriately substituted anilines by exhaustive alkylation with methyl sulfate for 1(a-R,M) and with ethyl bromide or ethyl sulfate for 2(a-R,M). Excellent yields were obtained in most cases in accord with the previous reports for similar reactions¹⁵ (Tables I and II).

The amine oxides were all synthesized by reaction of the tertiary amine with peracetic acid in chloroform. Reaction times varied for differently substituted anilines. Work-up for N,N-dimethylaniline oxides involved isolation and purification of the hydrochloride salts. The yields and selected physical properties of compounds prepared by this method are shown in Table III. Acceptable elemental analyses were obtained for the hydrochloric acid salts.

The substituted N,N-diethylaniline oxides were prepared using the conditions described for the dimethyl compounds, but the isolation procedure which yielded amine oxide hydrates was different and varied with the nature of the substituent. All of the substituted N,N-diethylaniline oxides were isolated as crystalline solids and all but one of

Table II Properties of *N*,*N*-Diethylanilines

		Lit Mn		Yiel	ield, % ^b	
Compd	Mp,°C or Bp,°C (mm)	°C or Bp,°C (mm)	PK_a^a	Meth- od 1	Meth- od 2	
2a		216°	6.58	87.4		
2b (<i>p</i> -OCH ₃)	147-149 (21)	246-247 ^d	7.22	71.5	90 [,]	
$2c (m-OCH_3)$	149(22)		6.29	98		
$2d(p-CH_3)$	123-125 (21)	229 ^s	6.92	80.6	90 ^f	
2e (<i>m</i> -CH ₃)	83 (4)	$231-231.5^{h}$	6.72	84.3	57.7	
2h (p -C1)	39	39 [#]		83.4	55.9	
2i (<i>m</i> -C1)	106 (5)	248249 ^s		92.3	43.4	
2] (p -Br)	32	33^i		79	65.6	
2 k (<i>m</i> -Br)	109 (3.3)	139,5– 142 ^j (9–10)			24.6	
$2m(m-NO_2)$	140 (5)	2 88–290*		79.8	10.6	

^a These values were determined from the half-neutralization points of titration curves of dilute solutions (<0.05 M). ^b In method 1 amine is heated with EtBr and base in an autoclave. In method 2 amine is neated with EtgSO₄ in aqueous base at reflux. ^c Commercially available — Aldrich no. D-8990-5. ^d D. G. Thomas, J. H. Billman, and C. E. Davis, J. Amer. Chem. Soc., 68, 895 (1946). ^e These pKa's were determined in 10::90 v/v alcohol-water solution. ^f These yields were determined by glpc of the ether extract of the reaction solution. Less than 1% of secondary amine was present. ^g R. Reinhardt and W. Staedel, Chem. Ber., 16, 29 (1883). ^h A. J. Hill and J. J. Donleavy, J. Ind. Eng. Chem., 13, 50 (1921). ⁱ A. Claus and H. Howitz, Chem. Ber., 17, 1327 (1884). ^j W. A. Jacobs and M. Heidelberger, J. Biol. Chem., 21, 127 (1915). ^k A. Groll, Chem. Ber., 19, 198 (1886).

these contained water of hydration, usually with a simple whole number ratio of water molecules to oxide. The presence of water and the amount of water per sample was measured by nmr, elemental analysis, and molecular weight calculated from acid-base titrations. The properties of these compounds are summarized in Table IV.

It was possible to isolate acetate or sulfate salts of the oxides. Analysis by nmr allowed a quick test for the absence of acetate salt that resulted if either too little base or water was used in the neutralization of the reaction mixture.

Discussion

Yields of alkylated amine are affected by the nature of the alkylating reagent and by the reaction temperature. The fact that methylation occurs readily at lower temperature whereas ethylation gave good yields of tertiary amine only when heated above 100° is in keeping with the known dependence of SN^2 reaction on the nature of the alkyl group. The syntheses were most convenient when the amounts of secondary amine remaining were minimized. Purification involved separation of tertiary amine from secondary amine and from the inevitable black tar.

The methylations could be driven completely to quaternary salt formation and the extra methyl group removed by steam distillation from strongly basic medium with no detectable amount of secondary amine contamination. It was, however, difficult to carry the diethyl sulfate alkylations beyond the point of mixtures of tertiary amine, quaternary salt, and unacceptably large amounts of secondary amine. Separation was accomplished by conversion of the secondary amine to amide with acetic anhydride. Ethylation in an autoclave with ethyl bromide usually gave good yields of tertiary amine without secondary amine contamination Preparation of N, N-Diethyl- and N, N-Dimethylaniline Oxides

Oxide Hydrochlorides					
	Yield,	Mp, °C	Mp, °C		-
Compd	%	(expt)	(lit.)	р <i>К</i> а	10 ⁵ K _a
3 a (H)	44	124-125	124–125 ^b	4.26°	$5.52 \pm$
3 b (<i>p</i> -OCH ₃)	37	144–145	146 ^b	4.34	4.58 ±
3c (<i>m</i> -OCH ₃)	20	109–111	112-113 ^b	4.16	6.89 ±
$3d(p-CH_3)$	52	124–125	138 ^b	4.34°	$4.52 \pm$
3е (<i>m</i> -СH ₃)	39	115–117		4.26	$5.55 \pm$
3f (<i>p</i> -F)	20	155-157		4.09	$8.11 \pm$
3g(m-F)	15	117-120		3.95	11.2^{f}
3h (<i>p</i> -Cl)	64	149-151	142–143 ^b	4.02	9.96 ± 0.21^{e}
3i (<i>m</i> -C1)	50	141–142		3.89	13.0 ±
3j (<i>p</i> -Br)	35	155–158	165-166 ^d	3.97	$10.7 \pm 0.9^{\circ}$
3k (<i>m</i> -Br)	48	142–144		3.86	13.88 ±
31 (<i>p</i> -NO ₂)	28	149-152	168-169 ^d	3.50	$31.3 \pm$
3 m (<i>m</i> -NO ₂)	45	146-148	157-158 ^d	3.47	2.1 31.9 ± 1.4

Table III Substituted N, N-Dimethylaniline Oxide Hydrochlorides

^a All compounds melted with decomposition. ^b R. Huisgen, F. Bayerlein, and W. Heydkamp, *Chem. Ber.*, **92**, 3223, (1959). ^c Reference 18 lists 4.21 for 1a and 4.32 for 1d. ^d L. W. Jones and E. B. Hartshorn, *J. Amer. Chem. Soc.*, **46**, 1845 (1924). ^e Average error in nine pH values from a single titration curve. ^f Single titration curve value of the half-neutralization point.

even for amines with deactivating substituents (*i.e.*, m-NO₂) and must be considered the preferable method.

Analysis for purity was most conveniently carried out by examination of the 3300-cm⁻¹ region of the ir spectra, although glpc and nmr gave equally unambiguous indications of the amounts of primary, secondary, and tertiary amines.

The synthesis of amine oxides using peracetic acid in chloroform provides good yield in a rapid reaction. This is consistent with the experience of Craig and coworkers¹⁶ using *m*-chloroperbenzoic acid. Diminished yields of crystalline products are caused by the extreme solubility of the oxide in water. An acceptable procedure involves extracting the oxide from aqueous base with chloroform. The distribution coefficient strongly favors water and is affected by the substituent. The first extract in chloroform contains a variety of organic impurities including starting amine and its other oxidation products. These can be removed from the solid amine oxide with ether or ether-hexane mixtures.

The white crystalline N,N-diethylaniline oxides were, with the exception of **2j**, all isolated as hydrates. The degree of hydration for each was determined by (1) titration of a known weight of amine oxide, (2) nmr in CDCl₃ (a broad singlet between δ 4 and 5) and (3) by elemental analyses which gave acceptable values only when calculated with water of hydration. The presence of the acetate salt, with the hydrate or instead of it, was easily ascertained by the characteristic nmr signal at δ 2.

The nature of the hydrate has an effect on the physical properties of the amine oxide and on the rates of reaction of the oxide function in nonhydroxylic solvents. We have observed, for example, that the acetate salts are more solu-

Table IVProperties of N, N-Diethylaniline Oxides

Compound	Yield, %	Mp,.°Ċ ^a	р ^к а ^b	H2O of hydra- tion	λ(N-O), cm ⁻¹ infra- red
4a	70	88–89°	4.50^{d}	1.5	961
$4b(p-OCH_3)$	36.0	80-82	4.66	0.5	945
$4c (m - OCH_3)$	24.5	86-87	4.46	0.5	950
$4d(p-CH_3)$	84.5	101	4.67	0.5	950
4e $(m - CH_3)$	68.5	99-100	4.64	1	957
4h(p-C1)	71.4	91-92	4.28	0.5	949
4i (<i>m</i> -C1)	13.8	105-106	4.21	1	955
4j (p-Br)	65.6	104	4.27	0.5	946
4k(m-Br)	51.6	8 2	4.14	е	984
41 (p -NO ₂)	26.4	91-92	3,80	2	949
$4m(m-NO_2)$	69.5	81-82	3.79	1	945

^a Compounds melted with decomposition. ^b All values were determined from the half-neutralization points of titration curves. All are averages of three runs except 2m and 2e (2 titrations) and 2h, 2i, and 2j (1 titration). ^c Reference 4 reports of 96° for the monohydrate. ^d Reference 18 reports a value of 4.53 for this compound. ^e Contains one acetic acid molecule rather than one water molecule per product molecule.

ble in nonpolar solvents, *i.e.*, benzene or chloroform than the hydrates. The hydrochlorides are insoluble in nonpolar solvents, may be crystallized from chloroform or low molecular weight ketones, and are soluble in all proportions in water or alcohols. The water of hydration can be removed at -70° in THF with molecular sieves, as found by Cram and coworkers.¹⁷ Once the water of hydration is removed, Cope elimination occurs even at room temperature.

The pK_a 's of the amine oxides correlate very nicely. The average deviation in each case was less than 7% of the K_a value. In most cases the average error is less than 3% which is of the same order of magnitude as the accepted errors in pH standard solutions and glass electrode potentials. The values of the pK_a 's also agree with those of Nylen,¹⁸ who



Figure 1. Hammett plot of the pK_a values of 3 and 4 vs. σ^n .

obtained values of 4.21 for 3a, 4.32 for 3d, and 4.53 for 4a. The substituted N_iN -dimethylaniline oxides were titrated as the hydrochlorides with sodium hydroxide. The titration curves were analyzed by computer program in a manner suggested by Albert and Sargeant¹⁹ to give the pK_a values listed in Table III.

The substituted N,N-diethylaniline oxides were dissolved in water to give ~0.05 M solutions which were titrated with 0.1 M hydrochloric acid solution. The pK_a 's of these compounds were determined from the half-neutralization points. Although the latter pK_a 's were determined with a minimum of data analysis, the spread of values and correlation of them appears to be as good as that for the more rigorously analyzed data.

The p K_a 's of 3 and 4 correlated very well with the σ^n of van Bekkum, Verkade, and Wepster²⁰ and even better with each other (Figure 1). This is exactly what would be expected of a basic atom insulated from the benzene ring by a second period tetravalent atom. The σ^n value for p-F is somewhat suspect as it is based on fewer and less applicable data than the values of the other substituents.²⁰ The magnitude of the ρ values for the correlations is very close to those observed for the similarly affected substituted benzenearsonic acids ($\rho = 0.95$) and substituted benzenephosphonic acids ($\rho = 0.76$) p K_a values.^{20,21}

Experimental Section

Nuclear magnetic resonance (nmr) data were obtained from a Varian Model T-60 spectrometer with Permalok accessory. The samples were run in $CDCl_3$ solution using tetramethylsilane as an internal standard. Infrared (ir) spectra were obtained from films for liquid samples or KBr pellets for solids using a Beckman IR-10 spectrophotometer. Gas-liquid phase chromatography (glpc) was carried out on a Varian Aerograph Model A-90P.

Anilines and solvents were used as obtained commercially. The peracetic acid and 98% hydrogen peroxide were obtained from FMC Corporation. Melting points and boiling points were uncorrected and obtained at atmospheric pressure unless otherwise indicated. Analyses were carried out by Galbraith Labs, Knoxville, Tenn. The compounds N,N- dimethylaniline, m- and p-N,N- dimethylanilines, and N,N- dimethylanilines, and N,N- diethylaniline were purchased from Eastman Organic Chemicals.

General Procedure for Preparation of N,N-Dimethylanilines (1). The compounds 1c, 1k, 1g, 1i, 1f, and 1b were prepared by the following method. See Table I for physical properties and yields.

N,N-Dimethyl-m-anisidine (1c). A mixture of 12.3 g (0.1 mol) of m-anisidine, 30 g (0.3 mol) of sodium carbonate, and 100 ml of water was treated repeatedly with 12.6-g (0.1 mol) portions of dimethyl sulfate with stirring until the reaction mixture became homogeneous. The reaction temperature was maintained below 40°. The solution was made strongly basic and steam distilled (excess base is necessary to hydrolyze the quaternary salt). The oily layer was separated, combined with ether extracts of the aqueous layer, dried, concentrated, and vacuum distilled to give a colorless oil, bp 66-68° (0.1 mm) [lit.²² bp 204-205° (740 mm)].

p -Bromo-N,N -dimethylaniline (1j). A 57% yield of 1j was obtained by the method of Wurster and Beran. 23

p-Chloro-N,N-dimethylaniline (1h). A 60% yield of 1h was obtained from the appropriate diazonium salt by the method of Ayling and coworkers.²⁴

Substituted N,N-Dimethylaniline Oxide Hydrochlorides (3). A solution of 3 ml (0.1 mol) of 90% hydrogen peroxide and one drop of concentrated HCl in 30 ml of chloroform was allowed to warm to reflux while 12 ml (0.1 mol) of acetic anhydride was added over 15 min. After the mixture was stirred for 1 hr, 0.1 mol of substituted N,N-dimethylaniline was added dropwise while the temperature was maintained below 10°. After the product warmed to room temperature it was extracted with several portions of water. The aqueous extracts were combined and washed twice with ether, and the water was removed from the product on a rotary evaporator. When most of the water was gone, 15 ml of concentrated HCl was added. Crystals of the salt appeared after further evaporation. The products were recrystallized from butanone or mixtures of butanone and chloroform. The products gave acceptable analyses for C, H, N, and Cl. Yields and melting points (with decomposition) are given in Table III.

General Procedures for the Preparation of N,N-Diethylanilines (2). All of the diethylanilines used in this study except pnitro-N,N- diethylaniline were synthesized by one of two general methods; either the autoclave method or the diethyl sulfate method.

m-Nitro-*N*,*N*-diethylaniline (2m) (Method 1). A mixture of 0.3 mol of ethyl bromide, 0.33 mol of sodium acetate, 20 ml of water, and 0.1 mol of *m*-nitroaniline was put in an autoclave. The mixture was heated at 160° for 4 hr then cooled to room temperature, added to 1 l. of water, and made basic to litmus with 10% KOH. The product was steam distilled and the distillate was extracted with ether. The ether solution was dried (MgSO₄), filtered, and evaporated to leave an oil, which was vacuum distilled to give a 79.8% yield of product, bp 140° (5 mm) (lit.²⁵ bp 288-290°).

N,N-Diethyl-m-toluidine (2e) (Method 2). Diethyl sulfate (1 mol), Na₂CO₃ (1 mol), m-toluidine (1 mol), and 150 ml of water were combined with stirring. Heat and CO2 evolution accompanied the addition of 200 ml of diethyl sulfate. The rate of addition was adjusted to moderate the reaction. After the initial reaction subsided, more Na₂CO₃ (0.5 mol) was added and the mixture heated to reflux for 24 hr. The mixture was treated with another 50 ml of diethyl sulfate and heated at reflux for another 24-hr period. The organic phase was separated and combined with three further ether extracts of the aqueous phase. The aqueous phase was basified and steam distilled. The ether extracts of the steam distillate were combined with the previous ether extracts and dried (Na_2CO_3) . The ether was evaporated, and glpc analysis was used to determine the amount of secondary amine remaining. If the product was free of secondary amine it was vacuum distilled. When secondary amine was present an ether solution of product was treated with excess acetic anhydride and a few drops of concentrated H_2SO_4 . After 3 hr the mixture was washed with excess 10% HCl. The combined acid washings were made basic, separated from the tertiary amine, and extracted with ether. The combined amine and extracts were dried (Na₂CO₃) and filtered, and the ether was evaporated. The product was vacuum distilled. The physical properties and yields are listed in Table II.

p-Nitro-N,N-diethylaniline (2b). The method of Behr and coworkers²⁶ was used to prepare this compound in 95% yield, mp 70° (lit. 77–78°).

Preparation of Dialkylaniline Oxides (4). Amine (0.1 mol) was dissolved in 150 ml of CHCl₃ and cooled to -70° . After 40 ml of 40% peracetic acid was added slowly, the reaction was allowed to warm to room temperature. The acid was neutralized with saturated Na₂CO₃. The phases were separated and the aqueous layer was washed three times with chloroform. The washings were combined with the organic layer, the solution was dried (Na₂CO₃), and the CHCl₃ was rotoevaporated, leaving a hygroscopic solid. White crystals were obtained by trituration of the solid with ether. The product was filtered from the ether and quickly stored in a desiccator. The nmr spectra of all the products except 4k showed a peak for water of hydration between δ 3.5 and 5.0. A listing of physical properties, yields, and degree of hydration are listed in Table IV.

Determination of the pK_a 's. All measurements were carried out at 25.0 \pm 0.2° and in dilute (0.5 *M*) solution.

The pK_a 's of Substituted N,N-Dimethylaniline Oxide Hydrochlorides (3). Dilute solutions of 3 were placed in a waterjacketed flask containing a stirring bar and situated over a magnetic stirrer to allow for complete mixing. Water from a constant temperature bath was circulated around the flask allowing the temperature to be maintained at 25.0 \pm 0.2°. A Heathkit recording pH meter fitted with Beckman glass and calomel electrodes was used to monitor the titrations. A 1 rpm synchronous motor which had been adapted to drive a vernier microburet was connected so that it started simultaneously with the recorder chart drive. In this way known amounts of base per unit time could be added to the solutions of 3 while the resulting change in pH was being recorded.

The method for calculating the pK_a values from the neutralization curves was taken from Albert and Sargeant and modified so that it could be carried out by computer. The data were the pH's of the solution at various degrees of neutralization (*i.e.*, 10%, 20%, etc.). Then the pK_a 's were calculated at each of the points by means of simple pH vs. pK_a relationship. The average values of the resulting pK_a 's and their average errors are given in Table III.

The pK_a 's of N,N-Diethylaniline Oxides (4). Solutions (0.05 M) or less of amine oxide were titrated with standard 0.1 M HCl. The pH values were determined on a Sargent Welch Model NX

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digital pH meter fitted with a combination electrode. The pK_a was taken to be equal to neutralization point. The results are listed in Table IV. Three or more titrations were used except where indicated. The precision of the results appears to equal the accuracy normally accepted for glass electrodes, pH meters, and commercial pH standards.

The pK_a 's of N,N-Diethylanilines (2). These values were obtained from titration curves of 0.001 M solutions of the aniline in a slight excess of HCl titrated with $0.001 \ M$ NaOH solution. If the amines were insoluble in water (less than 0.001 M), but soluble in a 10% (v/v) ethanol-water solution, then the same concentrations were used in that medium. The results are summarized in Table II.

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Registry No.-1a, 121-69-7; 1b, 701-56-4; 1c, 15799-79-8; 1d, 99-97-8; 1e, 121-72-2; 1f, 403-46-3; 1g, 2107-43-9; 1h, 698-69-1; 1i, 6848-13-1; 1j, 586-77-6; 1k, 168-62-0; 1l, 100-23-2; 1m, 619-31-8; 2a, 91-66-7; 2b, 15144-80-6; 2c, 92-18-2; 2d, 613-48-9; 2e, 606-46-2; 2h, 2873-89-4; 2i, 6375-75-3; 2j, 2052-06-4; 2k, 53142-19-1; 2m, 2216-16-2; 3a, 5882-46-2; 3b, 13330-09-1; 3c, 53142-20-4; 3d, 13330-17-1; 3e, 53247-79-3; 3f, 53142-21-5; 3g, 53142-22-6; 3h, 16657-26-4; 3i, 53142-23-7; 3j, 16657-27-5; 3k, 53142-24-8; 3l, 13330-12-6; 3m, 53142-25-9; 4a, 826-42-6; 4b, 53142-26-0; 4c, 53142-27-1; 4d, 53142-28-2; 4e, 53142-29-3; 4h, 22480-56-4; 4i, 53142-30-6; 4j, 53142-31-7; 4k, 53142-32-8; 4l, 24429-84-3; 4m, 53142-33-9; dimethyl sulfate, 77-78-1; diethyl sulfate, 64-67-5; manisidine, 536-90-3; m-nitroaniline, 99-09-2; m-toluidine, 108-44-1; m-bromoaniline, 591-19-5; m-fluoroaniline, 372-19-0; m-chloroaniline, 108-42-9; p-fluoroaniline, 371-40-4; p-anisidine, 104-94-9; aniline, 62-53-3; p-toluidine, 106-49-0; p-chloroaniline, 106-47-8; pbromoaniline, 106-40-1.

References and Notes

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Reactions of Dichlorine Heptoxide and of Acyl Perchlorates with Ethers¹

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Spectral and solubility properties of acyl perchlorates, prepared from silver perchlorate and acid chlorides, are consistent with covalent mixed anhydride structures and not with acylium salts. Acetyl perchlorate in carbon tetrachloride reacted with tetrahydrofuran to give 4-perchloratobutyl acetate and with epoxides to give vicinal acetoxy perchlorates. Isopropyl ether gave isopropyl perchlorate and isopropyl acetate whereas isopropyl pentyl ether gave isopropyl perchlorate and pentyl acetate. Dimethoxymethane gave methyl acetate and methoxymethyl perchlorate. Benzoyl perchlorate and N,N- diethylcarbamoyl perchlorate reacted with tetrahydrofuran to give the corresponding 4-perchloratobutyl esters. Dichlorine heptoxide in carbon tetrachloride reacted with tetrahydrofuran, trimethylene oxide, and 2,3-butene oxide to give 1,4-butane diperchlorate, 1,3-propane diperchlorate, and 2,3-butane diperchlorate, respectively. Ethyl ether gave ethyl perchlorate and a trace of ethyl acetate. Propyl ether gave propyl perchlorate and isopropyl perchlorate, whereas isopropyl ether gave isopropyl perchlorate and 2,2-diperchloratopropane. Dimethoxymethane and dichlorine heptoxide gave methyl perchlorate and methoxymethyl perchlorate.

Dichlorine heptoxide in carbon tetrachloride was shown recently to be an effective perchlorylating agent for alcohols² and for amines.³ The present paper deals with reactions of this little explored reagent and of related acyl perchlorates with ethers.

Acvl perchlorates⁴⁻⁶ have been used as acylating agents and are generally assumed⁷ to be perchlorate salts of acylium cations, RCO⁺ClO₄⁻. Solubilities in nonpolar solvents and spectral properties, which should readily differentiate between the salt structures and the corresponding covalent mixed anhydrides, RC(0)-OClO₃, have not been reported.

The present work includes the characterization of acyl perchlorates and their utilization in ether cleavages to prepare alkyl perchlorate derivatives.

Acetyl chloride was found to react on mixing with a suspension of silver perchlorate in carbon tetrachloride to give a solution of acetyl perchlorate. The yield, determined by nmr, was essentially quantitative. The nmr chemical shift of the compound, δ 2.27, is close to those of acetyl halides and anhydrides, whereas values reported for CH_3CO^+ salts⁸ are approximately δ 4.0. The infrared spectrum of acetyl perchlorate shows a normal carbonyl peak at 1825