nuclidine are approximately additive and lead to an average reduction in p*Ka* of 2.8 p*K* units per benzo substitution. This relationship is shown in Figure 2.

Experimental

Anhydrous HOAc was prepared by distillation from triacetyl borate following Eichelberger and LaMer (*5*). Analysis of the distillate by the method of Bruckenstein (*1*) revealed no detectable H_2O. The ~0.1*N* $HClO_4$ titrant in anhydrous HOAc was prepared by adding 5.1 ml acetic anhydride to 2.2 ml of 70% $HClO_4$ in 70 ml HOAc. The mixture was then diluted to 250 ml with HOAc and allowed to stand for several days before use. The NaOAc was dried at 110°C for 24 hr prior to the preparation of the standard solution.

The titrations were carried out in a constant temperature bath at 25° ± 0.5°C using a Leeds and Northrup Model 7403-A2 pH meter. A Leeds and Northrup #1199-72 glass electrode was used as the indicating electrode, and the reference electrode was a modified calomel electrode containing a saturated solution of NaCl, $NaClO_4$, and Hg_2Cl_2 in anhydrous HOAc (*4*).

Samples containing ~0.06 meq base in 20 ml HOAc were titrated with the $HClO_4$ titrant using a 10-ml microburet. Prepurified N_2, dried by passing through a Drierite drying tower and saturated with HOAc by bubbling through anhydrous HOAc, was passed over the solutions throughout the titrations.

The preliminary experiment was run in anhydrous HOAc with a Sargent S-300072-15 combination electrode. The *o*- and *m*-chloroaniline, used as references, were purified by distillation.

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Synthesis of Certain *l*-Menthol Compounds

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Several new optically active *l*-menthol derivatives are synthesized by several different techniques. The index of refraction, boiling or melting points, optical rotatory dispersion, infrared spectrum identification, and percent yield are reported.

l-Menthoxy compounds are of considerable interest because of their utility as monodentate probes in the determination of vicinal and chromophoric effects on the induced Cotton effect of the cobalt (III) *d-d* transitions (*3*). Several new *l*-menthoxy ligands have been synthesized and are reported herein. The synthesis and structural determination of transition-metal complexes of these ligands are presently being investigated in this laboratory.

Experimental

l-Menthoxypropanenitrile (I) was prepared by alkaline condensation of *l*-menthol with acrylonitrile using trimethyl benzyl ammonium hydroxide according to the method of Bruson (*1*). The colorless oil had a bp 108–110°/2 torr (lit bp 149°/10 torr). *l*-Menthoxybutanenitrile (II) was prepared from *l*-menthol and allyl cyanide by the same procedure as for (I). The colorless oil had a bp of 122–125°/2 torr. *l*-Menthoxypropanoic acid (III) was prepared by acid hydrolysis of (I) according to the general method for hydrolysis of alkoxypropanenitriles (*4*). The colorless oil had a bp of 130–133°/2.7 torr. *l*-Menthoxybutanoic acid (IV) could not be prepared by general methods of either alkaline (*2*) or acid (*4*) hydrolysis for alkoxynitriles. Instead, it was prepared by the reactions of sodium *l*-menthoxide and 4-chlorobutanoic acid according to the method used for the synthesis of *l*-menthoxyacetic acid (*5*). The straw-colored oil had a bp of 134–137°/2 torr. *l*-Menthoxyacetamide (V) was prepared by conversion of *l*-menthoxyacetic acid (Aldrich Co.) to the acetyl chloride with thionyl chloride (*6*) and subsequent conversion to the amide by bubbling ammonia gas through an ethereal solution of the acetyl chloride for 4 hr. The solid product was twice recrystallized from hot water and subsequently sublimed, mp (uncorrected) 71–72°. *l*-Menthoxyethylamine (VI) was prepared by reduction of (V) with lithium aluminum hydride (*7*). The colorless oil had a bp of 126–130°/6 torr. Physical properties of Compounds I–VI are shown in Table I.

Melting points were determined on a Hoover mp apparatus. IR spectra were measured from thin films of the neat liquid (a melt of the solid acetamide) between NaCl plates. Continuous ORD spectra from 580 to 210 nm were measured from 3.22 mg/l. ethanolic solutions on a Cary 60 spectropolarimeter using 1-cm quartz cells. All of the ligands exhibited plain negative Drude ORD spectra over these regions. Optical rotations at 578, 546, 436, 365, and 313 nm were rechecked on a Perkin Elmer 241 spectropolarimeter, using larger quartz cells (1 dm) at the same ligand concentrations. Specific rotations agreed with ±0.2% for both instrumental measurements. Satisfactory elemental analyses were obtained for all new compounds (Huffman Labs, Wheatridge, Colo., and Schwarzkopf Labs, New York, N.Y.).

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Table I. Physical Properties of *l*-Menthoxy Compounds

	IR, cm^{-1}							%
Compound	OH	C=O	N—H	C≡N	C—O—C	n_D^{22}	$[\alpha]^{22}_{578}$	Yield
I				2240	1110	1.4586	−93.1	43
II				2230	1110	1.4601	−96.8	44
III	2960 925	1720			1115	1.4672	−74.0	72
IV	2900 910	1690			1110	1.4690	−69.4	28
V		1660	3500 3420		1110		−96.3	72
VI			3350 1600		1110	1.4621	−67.2	76

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