1 to 2 days),[5] the paper was dried, and the ions were located photographically.[3]

As indicated in Fig. 1, the separability of rare earths increased with decreasing concentration of the supporting electrolyte, lactic acid. Although the mobility was great in about 1.5 *M* acid, Sc trailed the unseparated rare earths. In acid less than 0.1 *M*, electromigration produced slowly migrating, elongated zones. This migration behavior and the separability of the zones depended upon the selective sorbability of the ions by the paper. Separate chromatographic experiments showed that the sorbability of the ions increased with decreasing concentration of the lactic acid as has been found with Ca.[5]

In 0.1 *M* lactic acid, the rate of separation of Y from Ce increased during the electrolysis. Various cations separated in the following sequence (decreasing mobility): Cs + Rb, Sr, Ca, Co, Zn, Cu, Sc, Y^{90} + Y^{91} + Nd, Ce + Pr + Pm + Eu, Hg + Zr + Nb. The Hg + Zr + Nb did not migrate, but if stabilized with oxalate Zr + Nb migrated to the anode.

With diammonium tartrate (0.015 *M*) plus tartaric acid (0.035 *M*), Ce(III) migrated as a cation, Eu and Pm as anions (Fig. 1). The separability and the sign of the ionic charge depended upon tartrate concentration and *p*H. Separability was not due to sorbability by the paper.

As determined by photography,[5] separation of many binary and ternary mixtures was complete. These mixtures included parents and daughters as Nd–Pm, Ce–Pr, Ba–La, and Sr-Y.

Combination of electrical migration with transverse flow of solvent, as previously described,[3] has now provided continuous separation of alkalies and alkaline earths from the rare earths. It has also yielded continuous separations of Y from Ce and of the rare earths from anions such as $PO_4^{\equiv}$.

[5] T. R. Sato, W. Kisieleski, W. P. Norris and H. H. Strain, *Anal. Chem.*, submitted.

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THE PEROXIDE AND LIGHT INDUCED REACTIONS OF AMINES WITH OLEFINS: A ONE-STEP SYNTHESIS OF *d,l*-CONIINE

Sir:

A reaction of considerable potential usefulness in organic synthesis, the addition of alkyl amines to olefins, has been observed. In the presence of a peroxide, a condensation occurs between the α-carbon atom of the amine and the olefin (the terminal carbon atom of 1-olefins) by what is probably a free-radical, chain reaction. For example, the reaction of piperidine with octene-1 in the presence of *t*-butyl peroxide gives 2-*n*-octylpiperidine, and *d,l*-coniine is obtained by the similar reaction of piperidine with propylene.

Under a pressure of nitrogen (25 lb./in.²), a reaction mixture containing piperidine (382. g., 4.50 moles, b.p. 105–106°, n^{20}D 1.4529), octene-1 (40 g., 0.36 mole, b.p. 120°, n^{20}D 1.4090), and *t*-butyl peroxide (3 g.) was held at 120° for 50 hours. Additional peroxide (2 g. after 6 hours, 2 g. after 12 hours) was added. Distillation of the reaction mixture gave *t*-butyl alcohol (6.3 g., b.p. 80–82°), unreacted piperidine (359.5 g., b.p. 103–105°), octene-1 (9.5 g., b.p. 118–120°), and a product shown to be 2-*n*-octylpiperidine (31.7 g., b.p. 89° at 1 mm., n^{20}D 1.4589).

Anal. Calcd. for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10; mol. wt., 197. Found: C, 79.34; H, 13.81; N, 7.17; mol. wt., 190.

This product was identified by a comparison of its chemical and physical properties with 2-*n*-octylpiperidine (b.p. 89° at 1 mm., n^{20}D 1.4587) prepared (95% yield) by the dehydrogenation (over Adams catalyst in acetic acid solution) of 2-*n*-octylpyridine (prepared, 65% yield, by the reaction of α-picoline, 111 g., 1.2 moles, with *n*-heptyl bromide, 71.6 g., 0.40 mole, and sodamide, 54 g., 1.39 moles).[1] The product gave a hydrochloride (m.p. 155–156°; m.p. of mixture with authentic sample, 155–156°).

Anal. Calcd. for $C_{13}H_{28}NCl$: C, 66.67; H, 12.07; N, 5.99. Found: C, 66.53; H, 12.16; N, 5.99.

Its reaction with phenyl isothiocyanate gave a thiourea derivative (m.p. 95°; m.p. of mixture with authentic sample, 95°). *Anal.* Calcd. for $C_{20}H_{32}N_2S$: C, 72.23; H, 9.70; N, 8.42. Found: C, 71.92; H, 9.56; N, 8.45.

A picrate (m.p. 78–80°) was also obtained. *Anal.* Calcd. for $C_{19}H_{30}N_4O_7$: N, 13.12. Found: N, 13.07.

The high boiling residue was distilled to give a fraction (b.p. 145–155° at 1 mm., n^{20}D 1.4683; 5.8 g., mol. wt. 299) presumed to have resulted from the condensation of one molecule of piperidine with two of octene-1. A residue (4.5 g., mol. wt. 448) remained. 2-*n*-Octylpiperidine (1 g.) was obtained in small yield when a solution containing piperidine (207 g., 2.44 moles) and octene-1 (20.5 g., 0.183 mole) was internally illuminated for 168 hours with a mercury discharge tube.

Piperidine (87. g., 1.03 mole) containing *t*-butyl peroxide (1.2 g.) was held at 125° for 12 hours under a pressure of propylene (30–40 lb./sq. in.). Additional peroxide (1.8 g.) was added as the reaction progressed. Distillation of the reaction mixture gave *d,l*-coniine (4 g., n^{23}D 1.4513, b.p. 93° at 70 mm.).[2,3] This product was identified by its hydrochloride (m.p. 211–212° uncor.) and its platinichloride (m.p. 155–157° uncor.). Work to determine the scope and mechanism of this reaction is continuing.

[1] A. E. Tchitchibabin, *Bull. soc. chim.*, (5) **5**, 429 (1938).
[2] E. Lellman and W. W. Muller, *Ber.*, **23**, 684 (1890).
[3] A. Ladenburg, *ibid*, **26**, 855 (1893).

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STEROID RING CLOSURES USING THE ACYLOIN CONDENSATION

Sir:

We have found that the acyloin condensation in a homogeneous liquid ammonia-ether solution is an