

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, Y⁹⁰ + Y⁹¹ + 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 *pH*. Separability was not due to sorbability by the paper.

As determined by photography,⁶ 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 alkalis 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 PO₄⁼.

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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*_D²⁰ 1.4529), octene-1 (40 g., 0.36 mole, b.p. 120°, *n*_D²⁰ 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*_D²⁰ 1.4589).

Anal. Calcd. for C₁₃H₂₇N: 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*_D²⁰ 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 C₁₃H₂₈NCl: 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 C₂₀H₃₂N₂S: 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 C₁₉H₃₀N₄O₇: 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*_D²⁰ 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*_D²⁰ 1.4513, b.p. 93° at 70 mm.).^{2,3} This product was identified by its hydrochloride (m.p. 211–212° uncor.) and its platinum chloride (m.p. 155–157° uncor.). Work to determine the scope and mechanism of this reaction is continuing.

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STEROID RING CLOSURES USING THE ACYLOIN CONDENSATION

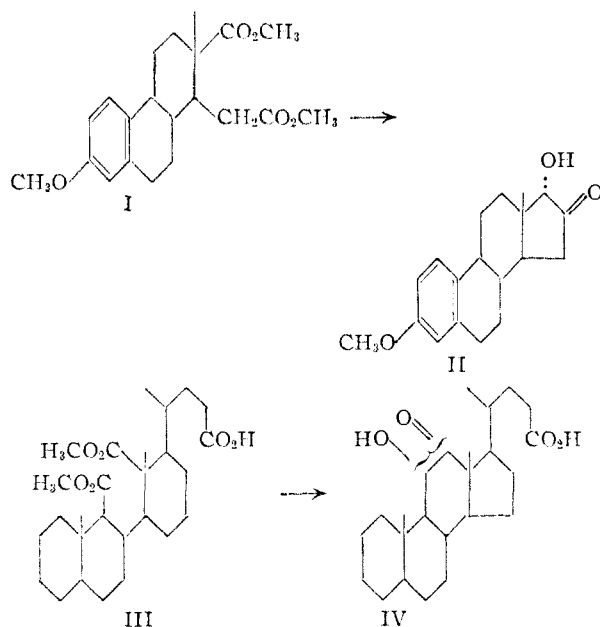
Sir:

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

efficient method of forming five- and six-membered rings. Sodium in liquid ammonia has not previously been considered to lead to practical yields of acyloins from esters.¹

To a solution of 0.8 g. of sodium in 325 ml. of anhydrous ammonia and 225 ml. of ether (under pre-purified nitrogen) was added in one hour 1.8 g. of dimethyl marrianolate methyl ether (I)^{2,3} dissolved in 225 ml. of ether. After complete removal of the ammonia by evaporation, the mixture was acidified with hydrochloric acid. Purification afforded 0.890 g. (60%) of 16-keto- α -estradiol-3-methyl ether (II), m.p. 162.0–162.4°, $[\alpha]_D^{25} -88^\circ$ ($c = 1.0$, 95% ethanol). *Anal.* Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.79; H, 8.09. Conventional heterogeneous acyloin reaction conditions (e.g., finely dispersed sodium in refluxing xylene) did not yield detectable quantities of acyloin product from I.

The acyloin II and II acetate showed a depression of m.p. on admixture with 16-keto- β -estradiol-3-methyl ether⁴ and the corresponding acetate, respectively. Reduction of II acetate by the ethanedithiol-Raney nickel method,⁵ followed by saponification and chromic acid oxidation, afforded estrone methyl ether, identified by comparison with an authentic sample.



By the same technique, 11,12-seco-cholane-24-acid-11,12 dimethyl ester (III) was cyclized in 75–80% yield to an 11,12-acyloin (m.p. 142–143°), identical with the lower melting ketol prepared by Reichstein's procedure⁶ (bromination of 12-keto-

cholanic acid and subsequent alkaline hydrolysis). The non-crystalline diester III was obtained by nitric acid oxidation of 12-hydroxycholanic acid or by chromic acid oxidation of an 11,12-acyloin mixture to 11,12-seco-cholane-11,12,24-triacid^{7,8} (m.p. 259–261°), followed by esterification with diazomethane and selective saponification. *Anal.* Calcd. for $C_{26}H_{42}O_6$: C, 69.30; H, 9.40; neut. equiv., 450. Found: C, 69.28; H, 9.25; neut. equiv., 446.

In other experiments employing a ratio of four equivalents of sodium to one of the diesters, the consumption of sodium appeared to be instantaneous. In each series only one of the four possible isomeric acyloins was obtained.

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CRYSTAL STRUCTURE OF CYANURIC ACID

Sir:

The infrared spectra of cyanuric acid and deuterocyanuric acid, which were recently published in THIS JOURNAL, by Newman and Badger,¹ create doubts concerning the values of the interatomic distances found in an early X-ray structure determination by Moerman and Wiebenga.²

The crystal structure of cyanuric acid was re-investigated in our laboratory by G. A. Croes, A. J. van Gent, R. P. van Oosten and D. W. Smits about two years ago. They started from new accurate measurements of the intensities of all X-ray reflections and refined the atomic coordinates by three dimensional Fourier syntheses. This work is not yet published, because we still want to study certain details of the electron density distribution. In connection with Newman and Badger's work, however, it may be interesting to report here the new values for the bond lengths. These are subject to a standard deviation of approximately 0.02 Å., which means that the probability that a given bond length is in error by more than 0.04 Å., or a bond angle by more than 3° is approximately 5%.

The molecules are all planar and situated almost exactly in parallel sheets (101). The old and new interatomic distances and bond angles are shown in Fig. 1 and Fig. 2, respectively, which show one molecule and its connections to others in the same layer.

The deviation from a trigonal symmetry of the central ring (Fig. 1) has disappeared (Fig. 2); the C–N bond lengths in the ring have practically not changed and are still all essentially identical.

On the other hand, a striking difference is observed between the new C=O distances and those previously reported. In the previous structure determination, which was based on estimated intensities and the use of the trial and error method only, we found two different C=O distances (1.24 Å. and 1.31 Å.), each with an estimated probable error of 0.06 Å., so that the difference was not

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