207–208°, was obtained. A mixed m.p. of the picrate with the free base was depressed to 150–170°.

Anal. Calcd. for $C_{15}H_{15}N_5O_8$: N, 17.81. Found: N, 17.97.

2-Methyl-5,6-trimethylenepyrimidol-4 (2-Methyl-6,7-dihydrocyclopentapyrimidol-4).—The general procedure was used with 10 ml. of ethanol, 0.47 g. of acetamidine hydrochloride and 0.78 g. of 2-carbethoxycyclopentanone[4] (b.p. 99–100.5° (10 mm.)). The reaction time was 12 hours at 25° plus 3.5 hours at reflux temperature. The extraction solvent was ethyl acetate. On cooling, the extract deposited long colorless needles. These when collected, washed with a little ethyl acetate, and dried, weighed 180 mg., m.p. 208–212°. From the filtrate by partial evaporation 54 mg. more material, of m.p. 207–212°, was obtained, making the total yield 234 mg. (31%).

The material sublimed easily at 2 mm. (125° bath), but this did not improve the purity. Repeated recrystallization of the material from ethyl acetate raised the m.p. to 214.5–215.5°. Analysis indicated that the compound was still not entirely pure, but it gave a picrate of satisfactory purity.

Anal. Calcd. for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.66. Found: C, 64.91; H, 7.10; N, 19.36.

4-Hydroxy-2-methyl-5,6-trimethylenepyrimidinium Picrate.—The crude picrate, prepared as described for the above quinazoline, was obtained in 51% yield, m.p. 178.5–182.5°. After recrystallization from *n*-butanol it melted at 184.5–185°.

Anal. Calcd. for $C_{14}H_{13}N_5O_8$: C, 44.33; H, 3.45; N, 18.47. Found: C, 44.11; H, 3.84; N, 18.29.

2-Carbethoxy-4-methoxycyclohexanone.—Hydrogenation[5] of commercial 4-methoxyphenol gave a *cis–trans* diastereomeric mixture of **4-methoxycyclohexanol**, b.p. 98–107° (15 mm.), in 89% yield.

The product was oxidized according to the procedure of Helfer[6] but to obtain the reported yield it was necessary to reduce the proportion of dichromate to a slight excess. **4-Methoxycyclohexanone** was obtained in 50–55% yield as a colorless liquid, b.p. 82–83° (13 mm.). A sample was converted to the 2,4-dinitrophenylhydrazone, m.p. 147–148° (reported[7] 150°).

The method of Cook and Lawrence[8] for the preparation of **2-carbethoxyformyl-4-methoxycyclohexanone** was modified as follows: The mixture of 4-methoxycyclohexanone (11.4 g.) and diethyl oxalate (14.7 g.) was added *to* the solution of sodium ethoxide in absolute ethanol (distilled from sodium). The reaction was conducted at 0–5° under dry nitrogen. After 2–3 hours stirring at 0°, the mixture was left overnight (with stirring), and after chilling to 0° was acidified and extracted.

The decarbonylation procedure[8] was modified by adding 100 mg. of powdered glass and 10 mg. of powdered iron to the entire batch of crude diketo-ester (a viscous oil), heated in a Claisen flask at 190°. The vigorous evolution of carbon monoxide was complete in 20 minutes, and 4.42 g. (25%, based on methoxycyclohexanone) of **2-carbethoxy-4-methoxycyclohexanone**, b.p. 128–135° (14 mm.), was obtained. On redistillation the product was obtained as a colorless liquid (3.69 g.), b.p. 139–141° (18 mm.) (reported[8] 131–133° (10 mm.)), $n^{20}{}_D$ 1.4783, D_{20} 1.102, $M^{20}{}_D$ 51.40 (theor. 49.50). The product gave a 2,4-dinitrophenylhydrazone of m.p. 125–128° dec., reported[8] 129–131° dec.

6-Methoxy-2-methyl-5,6,7,8-tetrahydroquinazolinol-4 Hydrochloride.—The general procedure was used with 0.47 g. of 2-carbethoxy-4-methoxycyclohexanone. The reaction time was three days at 25°. The extraction solvent was absolute ethanol. The hot filtered extract was cooled to 0°. Dry hydrogen chloride was passed into the solution for ten minutes. The colorless crystalline precipitate was collected, washed with ethanol and dried, giving 0.62 g. (54%) of product, m.p. 217–220° dec. After recrystallization of the product from absolute ethanol the m.p. was 221–222° dec.

Anal. Calcd. for $C_{10}H_{15}ClN_2O_2$: C, 52.06; H, 6.55; N, 12.15. Found: C, 52.24; H, 6.94; N, 12.15.

In earlier experiments the free base was isolated from the reaction mixture as colorless crystals, m.p. 129–137°. The yield was only 12% and purification was difficult.

5-Carbethoxymethyl-2,6-dimethylpyrimidol-4.—The general procedure was used with acetamidine hydrochloride (0.47 g.), 10 ml. of ethanol and 1.08 g. of diethyl acetosuccinate[9] (b.p. 103.5–106.5° (1 mm.), $n^{20}{}_D$ 1.4348, $M^{20}{}_D$ 52.22 (theor. 52.81). The reaction time was three days at 25°. The extraction solvent was ethyl acetate. The colorless crystals which separated from the extract were collected, washed (ethyl acetate) and dried, weight 159 mg. The filtrate on vacuum distillation to half-volume and dilution 1:1 with benzene gave 24 mg. more, making the total yield 182 mg. (18%), m.p. 177–179.5°. After recrystallization of the product from ethyl acetate–benzene (1:1) the m.p. was 181.5–182°.

Anal. Calcd. for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.33. Found: C, 57.80; H, 6.59; N, 13.39.

5-Carbethoxymethyl-2-hydroxymethyl-6-methylpyrimidol-4.—The general procedure was used with 1.10 g. of hydroxyacetamidine hydrochloride[2] (m.p. 147–148.5°), 22 ml. of ethanol and 2.16 g. of diethyl acetosuccinate.[9] (The amidine HCl was predissolved in half of the ethanol at the b.p.) The reaction time was 24 hours at 25° followed by 3 hours refluxing. The extraction solvent was 40 ml. of benzene (refluxed 20 minutes). The hot filtered extract on cooling deposited colorless needles which were collected, washed (benzene), and dried, giving 330 mg. (15%) of product, m.p. 137–142°. Repeated recrystallization of the product from benzene raised the m.p. to 143–144.5°.

Anal. Calcd. for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.39. Found: C, 52.48; H, 6.03; N, 11.61.

On heating with hydrazine hydrate the ester yields a colorless crystalline hydrazide, which can be recrystallized from ethanol and melts at about 225° (rapid heating), but which has not yet been purified sufficiently for analysis.

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RECEIVED SEPTEMBER 21, 1951

Anion Exchange Studies. IV.[1,2] Cobalt and Nickel in Hydrochloric Acid Solutions

BY GEORGE E. MOORE AND KURT A. KRAUS

The anion exchange behavior of nickel(II) and cobalt(II) in 0.5 to 12 *M* hydrochloric acid was studied by measuring their elution constants $E = dA/V$, where d is the distance (cm.) an absorption band moves when V (cc.) of eluent have been passed through a column of A (cm.^{2}) cross-sectional area.

Glass columns of the practically colorless resin Dowex-1 (a "strong base" quaternary amine polystyrene–divinylbenzene resin) were used, whose cross-sectional areas were 0.023 cm.^{2}. Since both nickel and cobalt are colored (the latter has a characteristic blue color on the resin) the band positions (and hence E) were determined visually. Approximately 1 mg. of Co and Ni were used per experiment. In addition a few experiments were carried out with tracer cobalt (Co^{60}) and d determined with the automatic scanner previously described.[3]

The results for cobalt are summarized in Fig. 1. E_{Co} rapidly decreases from approximately 2.5 in less than 3 *M* HCl to *ca.* 0.02 in 9 *M* HCl and

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(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper: K. A. Kraus and G. E. Moore, THIS JOURNAL, **73**, 2900 (1951).

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then increases again to *ca.* 0.055 in 12 *M* HCl. E_{Ni} on the other hand was found to be *ca.* 2.5 throughout the whole acid range. The difference in the adsorption behavior of the two elements is sufficient to permit excellent separation. Since as discussed earlier[3] $E = 1/(i + D)$ where i is the fractional interstitial space and D the distribution coefficient (amount per ml. of resin/amount per ml. of solutions), small values of E indicate good adsorption. Furthermore, E will reach a maximum value ($E_{\max} = 1/i$) when D becomes zero. Using sodium and potassium tracers and assuming that their ions are not adsorbed $E_{\max} = ca.\ 2.5$ was found for these columns. Hence there is negligible adsorption of nickel in the range 0.5 to 12 *M* HCl and of cobalt in the range 0.5 to 3 *M*.

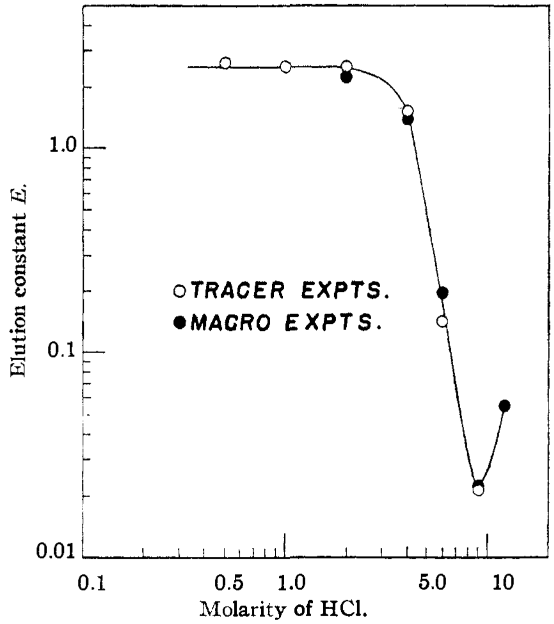

Fig. 1.—Adsorption of cobalt on Dowex-1.

Cobalt is adsorbed as a blue band which is sufficiently intense to permit detection of traces of cobalt (0.5 microgram in 9 *M* HCl was detectable on a 0.023 cm.[2] column). Such tests have also been carried out as batch experiments. For example, 1 mg. of Dowex-1 was stirred into 0.5 cc. of 9 *M* HCl containing 4 mg. of reagent grade $NiCl_2 \cdot 6H_2O$ (with 0.13% cobalt). The suspension was slowly dropped onto filter paper. A blue ring of resin (indicating cobalt) formed as the green solution dispersed through the paper.

A comparison of the adsorption data of cobalt with those of iron(III)[4] is of interest. The latter shows very much greater adsorption in concentrated HCl and no maximum as does cobalt near 9 *M* HCl. It had been shown earlier[3] that very strong adsorption in concentrated HCl is probably characteristic of singly negatively charged complex ions and that doubly (or higher) negatively charged complexes in this medium are relatively poorly adsorbed. The adsorbed ion in the case of iron has been identified with $FeCl_4^-$ through resin-capacity measurements,[5] further supporting the earlier conclusions. Additional evidence for the reasonably general applicability of this rule comes from the observation that gallium (probably as $GaCl_4^-$) is adsorbed quantitatively similarly to iron ($FeCl_4^-$).[6] One might thus tentatively assume that $FeCl_4^-$ and $CoCl_3^-$ are also approximately equally strongly adsorbed. On this basis the fraction of cobalt as $CoCl_3^-$ can be estimated to be considerably less than 1% even in 9 *M* HCl, the adsorption maximum.

Since in concentrated HCl a negatively charged complex of cobalt almost certainly exists in considerable concentration[7,8,9] one can conclude that it is not strongly adsorbed. Since this ion probably has a charge of minus two ($CoCl_4^{=}$)[7,8] this relatively poor adsorption in concentrated HCl is in general agreement with the earlier conclusion that in this medium only singly negatively charged complexes are extremely strongly adsorbed.

The non-adsorbability of Ni(II) by the resin suggests very strongly that negatively charged complexes of this element are not formed in appreciable concentration even in concentrated hydrochloric acid.

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Received July 18, 1951

Ethyl α,α-Dibromo-γ,γ,γ-trifluoroacetoacetate

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Although the preparation of ethyl γ,γ,γ-trifluoroacetoacetate was described some time ago,[1] little seems to be known of its α-halogenated derivatives. The preparation and properties of ethyl α-chloro-γ,γ,γ-trifluoroacetoacetate are described by Hill, Towne and Dickey.[2] The bromination of ethyl γ,γ,γ-trifluoroacetoacetate is mentioned by Henne and Mencher,[3] but no details are given.

Ethyl α,α-dibromo-γ,γ,γ-trifluoroacetoacetate has been prepared by the bromination of ethyl γ,γ,γ-trifluoroacetoacetate in the presence of pyridine, using (a) bromine itself, and (b) pyridine perbromide hydrobromide.[4] Both methods gave essentially the same rather low yield of product. In view of the facile chlorination of ethyl γ,γ,γ-trifluoroacetoacetate,[2] perhaps the simpler direct treatment of the ester with bromine would be effective, but as no further work on this compound is contemplated, our data are presented now. The considerable fore-run obtained in the distillations probably represents products formed by cleavage of the ester. Ethyl α,α-dibromo-γ,γ,γ-trifluoroacetoacetate is a colorless, mobile liquid, with a slight, but not unpleasant, odor (in contrast to

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