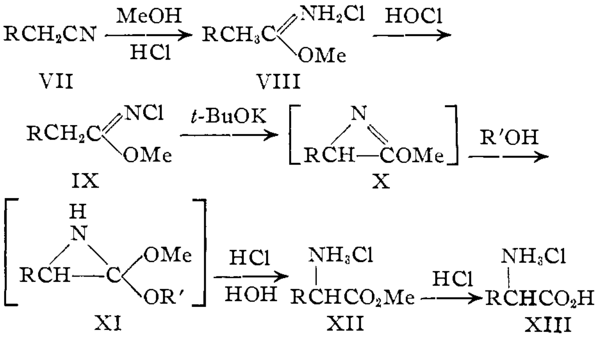
We have repeated Campbell's experiments obtaining a 57% yield of benzylphenylketimine hydrochloride. This material was converted to the free ketimine (IVa) by treatment with ammonia and the IVa was chlorinated and treated with methanolic sodium methoxide without isolation of either IVa or Va following the procedure reported previously[1] but using one-half the quantities of *t*-butyl hypochlorite and sodium methoxide. From the acidification of the reaction mixture with hydrochloric acid, desylamine hydrochloride was obtained in 66% yield, a yield that compared quite favorably with the 45% yield obtained from the rearrangement of N,N-dichloro-1,2-diphenylethylamine.[1]

By a procedure similar to that described previously[1] the azirine (or aziridine) intermediate in the rearrangement reaction was reduced with lithium aluminum hydride to form *cis*-2,3-diphenylethylenimine in 48% yield (based on the hydrochloride of IVa).

These two experiments taken together and with that of Alt and Knowles[4] would appear to establish fairly definitely that both the N-chloroketimine and the azirine (or some closely related aziridine derivative) are intermediates in the rearrangement of N,N-dichloro-*sec*-alkylamines.

Ethylphenylketimine (IVb) was prepared from the reaction of ethylmagnesium bromide with benzonitrile in approximately 65% yield[6] and subjected to the halogenation and rearrangement reactions, giving a 55% (36% over-all) yield of α-aminopropiophenone hydrochloride (VIb).



In the α-amino acid sequence a substituted acetonitrile (VII) is converted to the methyl imino ester hydrochloride (VIII); VIII is halogenated with aqueous hypochlorous acid to the N-chloroimino ester (IX), and IX is subjected to base-catalyzed rearrangement, possibly proceeding through the azirine (X) or aziridine (XI) intermediates, and subsequent acid hydrolysis to the methyl ester of the α-amino acid (XII). The considerable stability of the latter toward aqueous acid permits its isolation or, by more vigorous treatment, hydrolysis to the α-amino acid hydrochloride (XIII).

Although essentially the same reagents and conditions as described previously[1] could be used, best results were obtained when each step (except XII → XIII) was performed at ice-bath temperatures. This change necessitated the use of potassium *t*-butoxide for all but the more reactive N-chloroimino esters.

Any of the unbracketed intermediates could be isolated and purified (with due care) if desired but no intermediate needed to be so purified between the initial reactant (VII) and the selected final product (VI or VII).

In a typical example, propionitrile was converted with methanol and hydrogen chloride into methyl iminopropionate hydrochloride (VIII, R = CH_3) in 94% yield. Chlorination of the imino ester with aqueous hypochlorous acid[7] gave a crude chloroimino ester,[8] which was not purified but was rearranged by addition to a slight excess of potassium *t*-butoxide. Treatment of the rearrangement product with aqueous hydrochloric acid gave 58% (54% over-all) of methyl α-aminopropionate hydrochloride. Hydrolysis of the latter with hot hydrochloric acid gave alanine in 51% over-all yield.

Maximum over-all yields of other α-amino acids (as the hydrochloride) included: glycine, 51%, norvaline, 21%, leucine, 59%, phenylglycine,[9] 51%, and phenylalanine, 44%. In each instance the methyl ester could be obtained in yields about 4–5% higher than that for the acid. The yields in the rearrangement step (IX → X) varied from 51–70%.

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[6] Prepared by a procedure modelled after that of P. L. Pickard and T. L. Tolbert (private communication). We are indebted to Dr. P. L. Pickard for access to some of his unpublished results.

[7] Prepared from chlorine and a slight *excess* of aqueous sodium hydroxide.

[8] Chloroimino esters of the type described here show a strong band at about 6.2μ in the infrared spectrum and at most a weak band at 5.7μ (due to contamination by carboxylate ester).

[9] Sodium methoxide was used in place of potassium *t*-butoxide.

SYNTHESIS AND CHARACTERIZATION OF *CIS* AND *TRANS*-DICHLOROBIS-(ETHYLENEDIAMINE)-RHODIUM(III) SALTS:[1]

Sir:

We wish to report the synthesis and characterization of *cis*- and *trans*-$[Rh(en)_2Cl_2]^+$ salts (en = $NH_2CH_2CH_2NH_2$). None of the previous attempts to prepare geometrical and optical isomers of the dichlorotetramminerhodium(III) type had been successful. For example, salts of the complex ions $[Rh(NH_3)_4Cl_2]^+$,[2] $[Rh(en)_2Cl_2]^+$,[3] $[Rh(py)_4Cl_2]^+$,[4] $[Rh(bipy)_2Cl_2]^+$,[5] $[Rh(dien)_2Cl_2]^+$,[6] and $[Rh(en)(py)_2Cl_2]^+$[3] (py = pyridine, bipy = 2,2'-bipyridine, dien = $NH(CH_2CH_2NH_2)_2$) had been isolated in only one form and the structure of the particular isomer in each case was not established.

That these isomers had not been obtained and characterized previously is somewhat surprising

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)315. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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[6] F. G. Mann, *J. Chem. Soc.*, 469 (1934).

because the corresponding cobalt(III) compounds are well defined and have been known for a long time.[7] It is significant that the rhodium(III) isomers now have been prepared because it will be possible to make quantitative comparisons between these systems and the analogous cobalt(III) compounds. Work is now in progress on the kinetics and mechanism of hydrolysis, isomerization, and racemization of the rhodium(III) complexes.

The method described by Meyer and Kienitz[3] for the synthesis of $[Rh(en)_2Cl_2]Cl \cdot H_2O$ was tried several times but without success. Other attempts to prepare this compound also were unsuccessful.[8] The *cis*- and *trans*-$[Rh(en)_2Cl_2]NO_3$ finally were isolated from a reaction mixture obtained by gradually adding aqueous KOH to a refluxing water solution of $RhCl_3 \cdot 3H_2O$ and en·2HCl. In a typical preparation 1.0 g. of $RhCl_3 \cdot 3H_2O$ (0.0038 mole), 1.0 g. of en·2HCl (0.0076 mole), 0.43 g. of KOH (0.0076 mole) and 50 cc. of H_2O were heated to reflux. Over a period of 15 min. another 50 cc. of H_2O containing 0.43 g. of KOH (0.0076 mole) was added to the refluxing reaction mixture in 10 cc. increments. The color of this solution changed from dark red to bright yellow. Since the chloride salts are rather soluble and difficult to separate from KCl, 20 cc. of HNO_3 (concd.) was added to the cold reaction mixture after concentration to one half the original volume. Yellow-orange crystals of *trans*-$[Rh(en)_2Cl_2]NO_3$ separated in 33% yield (0.45 g.). *Anal.* Calcd. for $[Rh(en)_2Cl_2]NO_3$: C, 13.5; H, 4.53; Cl, 19.9. Found: C, 13.9; H, 4.63; Cl, 20.1. Evaporation of this filtrate to 20–30 cc. at room temperature yields 0.15 g. of bright yellow *cis*-$[Rh(en)_2Cl_2]NO_3$. Analysis of this isomer shows C, 13.9; H, 4.31; Cl, 20.0.

Although the chloride salts are fairly soluble, it has been possible to isolate *cis*- and *trans*-$[Rh(en)_2Cl_2]Cl$ from a reaction mixture of the type described above. When the reaction is finished, instead of adding HNO_3, the solution is concentrated. The first crystals to separate are the *cis* isomer after which the more soluble *trans* form is obtained from the mother liquor.

Assignment of the geometric configuration to the two isomers was made on the basis of the resolution of the asymmetric *cis* isomer. A solution of 0.45 g. of *cis*-$[Rh(en)_2Cl_2]Cl$ and 0.9 g. of *dextro*-ammonium α-bromocamphor-π-sulfonate in 15 cc. of H_2O was frozen in an ice–salt-bath. After melting, 0.25 g. of *l*-*cis*-$[Rh(en)_2Cl_2][d\text{-}C_{10}H_{14}O_4SBr]$ was collected on a filter and washed. This diastereoisomer was thoroughly ground with 2 cc. of a 1:1:1 mixture of ethanol:ether:HCl (concd.) and 0.19 g. of *l*-*cis*-$[Rh(en)_2Cl_2]Cl$ was isolated. The specific optical rotation of a 0.4% aqueous solution of this compound has values of $[\alpha]_{577m\mu}$ $-50°$ and $[\alpha]_{535m\mu}$ $-58°$.

Additional evidence in support of this structural assignment is offered by a comparison of the rhodium(III) isomers with the same cobalt(III) compounds of known structure. For example, the infrared spectra in the 3, 6, and 9 μ regions for the *cis* and for the *trans* isomers of the cobalt(III) and rhodium(III) complexes are almost identical whereas the spectra of the *cis* differ from those of the *trans* isomers.[9] Likewise the *cis*-chloride and *trans*-nitrate salts are the less soluble forms for the cobalt(III) and also for the rhodium(III) complexes. Finally, the rate of acid hydrolysis of *cis*-$[Rh(en)_2Cl_2]^+$ is faster than that of the *trans*-isomer as is also true for the analogous cobalt(III) complexes.

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SPIN DISTRIBUTION IN ALIPHATIC KETYLS[1]

Sir:

Electron spin resonance experiments confirm the conclusion of Favorsky and Nazarov[2] that hexamethylacetone and pentamethylacetone react with alkali metals to form free radicals. Reduction of solutions of the ketones in tetrahydrofuran by potassium yields products whose hyperfine splittings correspond to the free radicals containing the same numbers of protons as the original molecules. The spectrum of the ketyl of hexamethylacetone has seventeen lines evenly spaced at an interval of 0.12 oersted and symmetrically distributed about $g = 2.003$. The intensities correspond to hyperfine interaction with eighteen equivalent protons. Nineteen lines are expected, but the two weakest ones, of expected intensity only 2×10^{-5} as great as the strongest one, are not detected by our spectrometer. Pentamethylacetone yields a symmetrical doublet with splitting of 2.38 oe.; each member of the doublet is further split into incompletely resolved components with interval about 0.1 oersted.

The spectrum of each compound contains additional components whose intensities correspond well with those expected from splitting by C^{13} in its natural abundance. In hexamethylacetone two replicas of the central pattern are found symmetrically disposed about it (Fig. 1). The interval between the replicas is 7.6 oe., the intensity of each 0.033 that of the central pattern. A second pair of patterns, with intensity 0.17 of the first pair is found with splitting 49.6 oe. The intensity of the first pair corresponds to the 6.6% of the molecules which have one C^{13} in any of six equivalent positions, of the second pair to the natural abundance of C^{13} in a single position. We conclude that the splitting of 7.6 oe. arises from C^{13} in the methyl position, the 49.6 oe. from C^{13} in the central carbon. No splitting from the quaternary carbons is found. Similarly in pentamethylacetone the splitting by C^{13} in the central position is 49.8 oe. and by C^{13} in a methyl position 13 oe. Splitting by the five methyl carbons are approximately equal.

The large splittings by the central carbon atoms are in the same range as those in methyl radical[3]

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[1] This work was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract AF 49-638-469. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

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