powder (1.2 g.) carried out as described for the corresponding uranium(IV) compound. Dark brown crystals formed; m.p. 210° dec.

Anal. Calcd. for $V(C_{15}H_{11}O_2)_3$: V, 7.07. Found: V, 6.80.

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CONTRIBUTION FROM TEXACO EXPERIMENT,
INCORPORATED, RICHMOND, VIRGINIA

Hexahydroxylamminecobalt(III) Chloride and Fluoride

BY RUDOLPH C. WHITE AND S. W. FINLEY

Received May 4, 1964

Hexahydroxylamminecobalt(III) chloride has been prepared previously by Werner.[1] His procedure includes the reaction of free hydroxylamine with $(Co(en)_2Cl_2)Cl$. The method suffers from the disadvantage that small quantities of material must be used, and it involves the replacement of ethylenediamine, a strongly coordinated ligand, by hydroxylamine, a weaker, easily decomposed ligand. The method has been unreliable in our hands.

We have found that the general procedure of Bauer and Drinkard,[2] which uses $Na_3[Co(CO_3)_3]\cdot 3H_2O$ and amine hydrochlorides, can be adapted to the preparation of $[Co(NH_2OH)_6]Cl_3$. This procedure allows mild conditions to be used, which minimize the decomposition of free hydroxylamine. The preparation is best performed using small quantities of materials, and attempts to scale the reaction to larger quantities have been unsuccessful. However, the starting materials are widely available and the preparation is sufficiently rapid so that large amounts of the compound are readily accumulated.

The fluoride salt is obtained from the chloride by potentiometric titration with AgF. This is necessary in order to avoid an excess of silver ion, which decomposes the complex and is reduced to metallic silver.

The hexahydroxylamminecobalt(III) ion is relatively stable in acidic solution but rapidly decomposes in neutral or basic solution. The latter solutions are light-sensitive, and small amounts of impurities accelerate their decomposition. The pure compounds have been stored in the absence of light and moisture for periods of 2 years. It is interesting that the fluoride salt can be obtained quite readily free of hydrofluoric acid, whereas it is extremely difficult to obtain the amine salt in any form other than the acid salt.[3]

Experimental

Preparation of $[Co(NH_2OH)_6]Cl_3$.—Sodium triscarbonatocobaltate(III) trihydrate was prepared by the method of Bauer and Drinkard.[2] A solution of 4.2 g. of hydroxylamine hydrochloride dissolved in 20 ml. of 3 *N* HCl was added dropwise to a vigorously stirred slurry of 3.6 g. of the cobaltate in 10 ml. of water. The temperature was held between 0 and 5° during the addition. The cold mixture was stirred for 10 min., then cold concentrated HCl was added dropwise until leafy yellow crystals appeared. The mixture changed from muddy brown to blue-green when precipitation began. Filtration gave a crude brown product. Solution of this in the minimum amount of water and dropwise addition of concentrated HCl gave the pure hydroxylammine compound. Yields ranged from 10 to 15% of theoretical. The salt was extremely soluble, and unless the solutions were strongly acidic, severe decomposition resulted, with a corresponding decrease in yield. Concentrating the solution under vacuum gave slightly better yields.

Anal. Calcd. for $[Co(NH_2OH)_6]Cl_3$: H, 4.96; Co, 16.3; Cl, 29.3; N, 23.1. Found: H, 5.22; Co, 16.3; Cl, 27.9; N, 23.1.

Preparation of $[Co(NH_2OH)_6]F_3$.—A 3.5 *N* solution of AgF was prepared from Harshaw Spec. 101 grade material and was standardized against sodium chloride solution. A rapidly-stirred solution of 3.6 g. of $[Co(NH_2OH)_6]Cl_3$ in 30 ml. of 1 *N* HCl was titrated with 3.5 *N* AgF. The end point was determined potentiometrically, using a Beckman pH meter equipped with an Ag–AgCl and a calomel electrode. The observed end point agreed quite closely with the calculated amount of AgF required. It was necessary to avoid an excess of silver ion, as this appeared to promote decomposition of the complex. Filtration to remove AgCl gave a clear yellow solution, from which the fluoride salt was obtained by repeated addition of 2–3-ml. quantities of ethanol until precipitation was complete. The product was washed with alcohol and was dried over concentrated H_2SO_4. Yields averaged 50–60% of theoretical.

Anal. Calcd. for $[Co(NH_3OH)_6]F_3$: Co, 18.77; F, 18.15. Found: Co, 18.8; F, 18.2.

Analysis.—Cobalt was determined by an iodometric method similar to that outlined by McNabb for cobalt amines.[4] The sample was decomposed by heating in 6 *N* NaOH solution. Addition of 3% H_2O_2 to the cooled solution gave a precipitate of $Co(OH)_3$ which was filtered, washed, and dissolved in excess acidified KI solution. The liberated iodine was determined by titration with $Na_2S_2O_3$. Chloride was determined by potentiometric titration with $AgNO_3$. Fluoride was determined by precipitating as PbFCl.[5] This was separated by filtration, dissolved in 25% HNO_3, and chloride ion was determined by potentiometric titration with $AgNO_3$.[6]

Acknowledgment.—This work was supported by the Rocket Propulsion Laboratory, Air Force Systems Command, United States Air Force, Edwards Air Force Base, Calif.

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[2] H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

[3] R. W. Parry, D. R. Schultz, and P. R. Girardot, *ibid.*, **80**, 1 (1958).

[4] W. McNabb, *Z. anal. Chem.*, **92**, 7 (1933).

[5] F. Hawley, *Ind. Eng. Chem.*, **18**, 573 (1926).

[6] S. Bognar and L. Nagy, *Magyar Kem. Folyoirat*, **65**, 335 (1959).

CONTRIBUTION FROM BAKER LABORATORY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Spiro Silicon and Germanium Imidazolidines

BY C. H. YODER AND J. J. ZUCKERMAN

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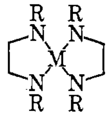
The reaction of germanium tetrachloride with ammonia[1] and various organic amines[1–4] has been known for over 30 years, but no studies of the action of difunctional organic amines have been reported. Ger-

TABLE I[a]

R	B.p., °C. (mm.), or m.p.	$n^{28}D$	Found Calculated, % C	H	N	M	Mol. wt.
			M = Si				
CH_3	75–76° (8)	1.4640	48.18	10.28	28.10	13.77	215[b]
			47.94	10.06	27.96	14.02	200
C_2H_5	123–124° (7)	1.4677	56.09	11.05	21.90	11.00	241[c]
			56.18	11.00	21.85	10.95	256
p-$CH_3C_6H_4$	300–304° (m.p.)		75.32	6.54	10.98	5.86	458[d]
			76.14	7.19	11.10	5.56	504
			M = Ge				
CH_3	106° (16)	1.4859	39.53	8.43	22.97	29.54	223[e]
			39.23	8.23	23.26	29.64	245
C_2H_5	140–142° (9)	1.4904	48.09	9.49	18.82	24.38	300[f]
			47.88	9.38	18.62	24.13	301
C_6H_5	305–310° (m.p.)		67.93	5.73	11.25	14.93	504[d]
			68.20	5.72	11.36	14.72	493
p-$CH_3C_6H_4$	317–320° (m.p.)		70.12	6.78	9.98	13.32	539[d]
			69.96	6.61	10.20	13.22	549

[a] Melting points were measured on a Townson and Mercer Type 5 melting point block and are uncorrected. Analyses were done by Schwarzkopf Microanalytical Laboratory and Scandinavian Microanalytical Laboratory. Refractive indices were measured on an Abbé refractometer. [b] Determined by osmometry in carbon tetrachloride. [c] Determined by Rast method. [d] Determined by osmometry in dibromomethane. [e] Determined cryoscopically in cyclohexane. [f] Determined cryoscopically in benzene.

manium tetrachloride reacts with a number of N,N′-disubstituted ethylenediamines to give spiro imidazolidines with germanium as the central spiro atom. The analogous silicon compounds were also prepared.

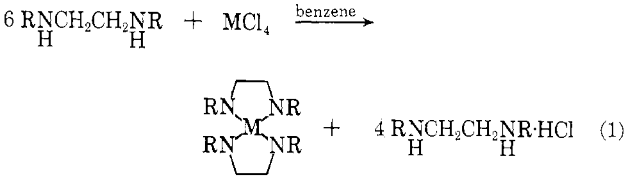


M = Si; R = CH_3, C_2H_5, p-$CH_3C_6H_4$
M = Ge; R = CH_3, C_2H_5, C_6H_5, p-$CH_3C_6H_4$

The analogous organic compounds (M = C) are not known. The spiro structure has been confirmed by infrared and n.m.r. spectroscopy. N.m.r. spectra of the alkyl compounds show a single sharp peak for the methylene bridge protons of the ring. This has been interpreted as indicating either planarity of the ring systems or the rapid inversion of tetrahedral nitrogen atoms.[5] The possibility that this is due to Si–N (p → d) π-bonding is being investigated.

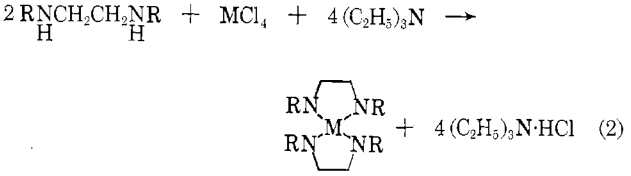
Physical properties and analytical data are given in Table I. The alkyl-substituted spiro imidazolidines are liquids, soluble in organic solvents, but the aryl derivatives in both the silicon and germanium series are white, crystalline solids only slightly soluble in most organic solvents. Purification was achieved through fractional distillation for the former type, but the arylgermanium compounds were recrystallized from pyridine, and the arylsilicon derivative was sublimed *in vacuo*. The compounds hydrolyze in moist air to regenerate the organic diamine: the germanium compounds are attacked more readily than the silicon with the N,N′-dialkylgermanium derivatives being particularly hydrolytically sensitive.

The N,N′-dialkyl compounds were prepared by the reaction of the corresponding diamine with the tetrachloride in benzene at 40–60°.



$$6\,R\underset{H}{N}CH_2CH_2\underset{H}{N}R + MCl_4 \xrightarrow{\text{benzene}} \ldots + 4\,R\underset{H}{N}CH_2CH_2\underset{H}{N}R\cdot HCl \quad (1)$$

Aryl derivatives were synthesized in the presence of triethylamine, using either benzene or dioxane as a solvent.



$$2\,R\underset{H}{N}CH_2CH_2\underset{H}{N}R + MCl_4 + 4(C_2H_5)_3N \longrightarrow \ldots + 4(C_2H_5)_3N\cdot HCl \quad (2)$$

The N,N′-dialkyldiamines gave the corresponding imidazolidines in reasonably good yield, but the yields with the aryl derivatives were very low (*ca.* 1%). The reaction of silicon tetrachloride with N,N′-diphenylethylenediamine produced a trace of material containing Si–N bonds, but purification proved impossible.

The reaction of N,N′-di-*o*-tolylethylenediamine with both silicon and germanium tetrachlorides did not proceed. Studies of models show that although the planar ring conformation is favored over the conformation involving tetrahedrally hybridized nitrogen, the N-*o*-tolyl spiro compound would be a very strained system in either case. Similar steric difficulties were encountered by Tansjö in the preparation of tris(N-methylanilino)-*n*-propylsilane.[6] Although tetrakis(*o*-tolylamino)silane was reported in the last century,[7] the

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(1) W. C. Johnson and A. E. Sidwell, *J. Am. Chem. Soc.*, **55**, 1884 (1933).
(2) J. S. Thomas and W. W. Southwood, *J. Chem. Soc.*, 2083 (1931).
(3) H. H. Anderson, *J. Am. Chem. Soc.*, **74**, 1421 (1952).
(4) R. Schwarz and W. Reinhardt, *Ber.*, **65**, 1743 (1932).
(5) D. Kummer and J. D. Baldeschwieler, *J. Phys. Chem.*, **67**, 98 (1963).
(6) L. Tansjö, *Acta Chem. Scand.*, **11**, 1613 (1957); **13**, 35 (1959).
(7) J. E. Reynolds, *J. Chem. Soc.*, **55**, 474 (1889).

difficulty encountered in the attempted formation of the *o*-tolyl spiro derivative is probably associated with the presence of both the *o*-methyl and the bridging N-alkyl groups.

An analogous silicon spiro compound [where R = Si-$(CH_3)_3$] has been synthesized recently by Kummer and Rochow, who indicated that the presence of the N–Si-$(CH_3)_3$ group was necessary for the formation of five-memberd rings by the reaction of chlorosilanes and ethylenediamines.[8] The present work shows that cyclic compounds can be obtained by the more general reactions 1 and 2 where R may be a variety of alkyl or aryl groups.

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It has come to our attention during the preparation of this note that the N-methyl and N-ethyl spirosilicon imidazolidines have been independently obtained through transamination by Dr. E. W. Abel and coworkers at the University of Bristol, England. We thank Dr. Abel for sharing his results with us.

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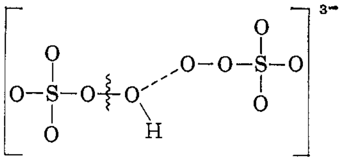
CONTRIBUTION FROM THE METCALF RESEARCH LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND

An Isotope Study of the Decomposition of Caro's Acid

BY E. KOUBEK, GERRIT LEVEY, AND JOHN O. EDWARDS

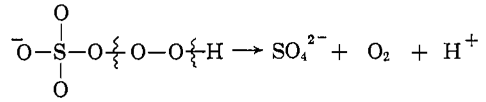
Received May 4, 1964

There has been considerable current interest in the mechanisms by which peroxides decompose. Ball and Edwards[1] reported a kinetic study on the aqueous decomposition of Caro's acid to give sulfate and oxygen. They suggested, on the basis of the rate law $R = k[HSO_5^-][SO_5^{2-}]$ and other evidence, a mechanism involving displacement on oxygen by oxygen involving an activated complex of the type



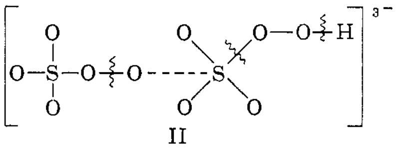
I

with dotted lines indicating bonds being formed and zigzag lines denoting bonds being broken. The intermediate HSO_6^- is presumed to decompose rapidly to oxygen, sulfate ion, and hydrogen ion.



$${}^{-}O-\overset{O}{\underset{O}{S}}-O\wr O-O\wr H \longrightarrow SO_4^{2-} + O_2 + H^+$$

Goodman, Robson, and Wilson[2] reported on a study of aromatic peroxy acid decomposition in aqueous solutions; they observed a rate law similar to the Caro's acid case, and they suggested a peroxy anion attack on the electrophilic carbonyl carbon of an un-ionized peroxy acid. They also suggested that this type of mechanism might hold for other peroxy acids including Caro's acid and this would involve (in its simplest form) an activated complex such as

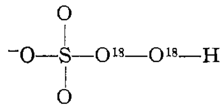


II

The original study[1] on Caro's acid has been repeated[3] and the alternative mechanism involving attack by peroxide oxygen on sulfur reiterated. Simultaneously, a study[4] of the decomposition of several peroxides was reported. Included were experiments involving double-labeled peroxyacetic acid, $CH_3C(=O)O^{18}O^{18}H$, in the presence of nonlabeled peroxyacetic acid; the results are consistent with a mechanism wherein a peroxyacetate ion attacks the carbonyl carbon of the un-ionized peroxy acid leading to an activated complex similar to type II.

In view of these observations and speculations, further study on the mechanism of the decomposition of Caro's acid seemed desirable. An experiment of the kind carried out earlier[4] using double-labeled peroxy acid was invoked in order to distinguish between the two suggested mechanisms (both of which are consistent with the rate law and other data) for the reaction between SO_5^{2-} and HSO_5^-. Mechanism I requires that one oxygen atom in each oxygen molecule originate from one peroxy anion; therefore, in the double-labeling experiment, scrambling of oxygen atoms is required and the O^{18} isotope will be predominantly in the O_2^{34} species. Mechanism II requires that both atoms in a product oxygen molecule come from the same peroxy anion so no scrambling is predicted; this was found to be the predominant (but not exclusive) product with peroxyacetic acid.[4]

We have now prepared a mixture of $KHSO_5$ species containing $\sim$1.1% double-peroxide-oxygen-labeled $KHSO_5$



$${}^{-}O-\overset{O}{\underset{O}{S}}-O^{18}-O^{18}-H$$

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[1] D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

[2] J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).

[3] J. F. Goodman and P. Robson, *J. Chem. Soc.*, 2871 (1963).

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