

We were unable to obtain a benzylidene derivative from I and benzaldehyde.

Upon alkaline hydrolysis I and II gave the corresponding mono- and dicarboxylic acids IV and V, in crystalline form. However, the tricyanoethylation product III gave a non-crystallizable acidic material under the same hydrolysis conditions.

Experimental

The isophorone used was the commercial product available from Carbide and Carbon Chemicals Corporation. If the material has stood in a partly filled bottle in the sunlight for more than a few months, it often fails to react with acrylonitrile even after redistillation. Apparently, peroxidic or acidic bodies are formed by autoxidation, which poison the catalyst. A similar phenomenon is shown by mesityl oxide² and other unsaturated ketones.

In order to purify the isophorone it was thoroughly washed with a 5% solution of sodium carbonate and then distilled under reduced pressure, immediately before use.

Cyanoethyl-isophorone (I).—To a stirred mixture of 276 g. of isophorone (2 moles), 200 g. of *t*-butyl alcohol and 3 cc. of "Triton B" (40% aqueous solution of benzyltrimethylammonium hydroxide) there was added dropwise during the course of one hour, 106 g. of acrylonitrile (2 moles) while maintaining the reaction temperature at 26–28° with water cooling. The mixture was stirred at 26–30° for 4 hours longer, then rendered slightly acidic with dilute hydrochloric acid, washed with water, the oil layer separated and distilled in vacuum.

After a forerun of 146 g. of material boiling up to 135° (1 mm.) had been removed, three separate fractions were collected as follows: (a) 52 g., b.p. 135–190° (1 mm.); (b) 95 g., b.p. 190–240° (1 mm.); (c) 27 g., b.p. 240–290° (1 mm.).

Fraction (a) upon redistillation gave 46 g. of a pale yellow oil, b.p. 115–120° (0.3 mm.). Upon redistillation through an 8-inch column, this yielded 35 g. of monocyanoethylation product, b.p. 109–111° (0.3 mm.), as a colorless oil, m.p. 23–24°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}$: N, 7.32. Found: N, 7.39.

Fraction (b) contains dicyanoethylated isophorone which, however, is obtained in better yield by using 2 moles of acrylonitrile for 1 mole of isophorone as given below.

Di-(cyanoethyl)-isophorone (II).—To a stirred mixture of 138 g. of isophorone (1 mole), 200 g. of *t*-butyl alcohol and 4 g. of "Triton B" there was added dropwise 106 g. of acrylonitrile during the course of one hour at 28–32° with cooling. After stirring 4 hours longer at 30° and working up as described above, the following fractions were collected: (a) 50 g., boiling up to 155° (1 mm.) (discarded); (b) 20 g., b.p. 155–210° (1 mm.) (mostly I); (c) 75 g., b.p. 210–220° (1 mm.); (d) 48 g., b.p. 220–295° (1 mm.). Fraction (c) crystallized on standing. Upon recrystallization from ethanol colorless crystals, m.p. 83°, were obtained; yield 53 g.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}$: N, 11.47. Found: N, 11.38.

Tri-(cyanoethyl)-isophorone (III).—Upon redistilling fraction (d), b.p. 220–295° (1 mm.), from the preceding preparation, there was obtained 24 g. of viscous reddish oil, b.p. 265–280° (1 mm.), which became partly crystalline when allowed to stand for several weeks with a small amount of ethanol in a refrigerator at 0–7°. The filtered solid material upon recrystallization from ethanol yielded 4 g. of colorless crystals, m.p. 120–121°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{23}\text{N}_3\text{O}$: N, 14.13. Found: N, 14.23.

Carboxyethyl-isophorone (IV).—A mixture of 19.1 g. of cyanoethyl-isophorone (I), 11.2 g. of potassium hydroxide and 100 g. of water was boiled under reflux for eight hours.

(2) R. L. Frank and J. B. McPherson, *ibid.*, **71**, 1387 (1949).

The clear solution was cooled and acidified with hydrochloric acid. The soft mass which precipitated became solid after stirring for a short time; yield 90%. After several recrystallizations from petroleum ether, the compound was obtained as colorless crystals, m.p. 76–77°.

Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{O}_3$: neut. equiv., 210. Found: neut. equiv., 209.

Di-(carboxyethyl)-isophorone (V).—A mixture of 12.2 g. of di-(cyanoethyl)-isophorone (II), 11.2 g. of potassium hydroxide and 90 g. of water was boiled under reflux for 18 hours. The clear solution was cooled and acidified with hydrochloric acid; crude product yield 9 g. After recrystallization from nitromethane, it formed colorless crystals, m.p. 181°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_5$: neut. equiv., 141. Found: neut. equiv., 140.2.

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Bis-cyclopentadienyl Compounds of Rhodium(III) and Iridium(III)

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The great stability of the unipositive bis-cyclopentadienylcobalt(III) (cobalticinium) ion¹ led us to attempt the preparation of the analogous bis-cyclopentadienylrhodium(III) and bis-cyclopentadienyliridium(III) cations. These ions, hereafter referred to as the rhodicinium and iridicinium ions, respectively, have been prepared and some of their properties determined.

Experimental

A benzene solution of the metal acetylacetonate² was added to a benzene solution of cyclopentadienylmagnesium bromide, the proportion being 10 moles of the Grignard reagent per mole of the acetylacetonate. Although the reaction appeared to take place immediately, as evidenced by the formation of a red-brown precipitate, the mixture was held at about 70° for 24 hours. It was then decomposed using an equal volume of ice slush. The mixture was filtered, and the yellow aqueous layer was separated. The aqueous solutions so obtained were extracted several times with ether and were made essentially free of magnesium by adding barium hydroxide to precipitate magnesium hydroxide, the barium being removed by adding an equivalent amount of dilute sulfuric acid. The organometallic ions were then precipitated with a solution of iodine in potassium iodide; after thorough washing, the precipitates were dissolved in 6 *N* nitric acid, the solutions were then boiled to remove iodine, and evaporated nearly to dryness to remove excess nitric acid. Solutions of salts of other anions such as chloride and perchlorate were obtained by passing the nitrate solutions through columns of anion-exchange resin (Dowex A2) in the appropriate form.

The rhodicinium and iridicinium ions and salts show chemical stability comparable to that of the cobalticinium analogs. Solutions of these salts can be evaporated almost to dryness with concentrated nitric acid without decomposition. In neutral or acid solution they seem quite stable toward light. They are, however, rather unstable in basic solution; a basic solution of rhodicinium ion becomes cloudy after a few hours at room temperature and develops a fluffy white precipitate after a few seconds of boiling. In order to analyze for the metal, the compounds can be decomposed by fuming with perchloric acid.

The rhodicinium and iridicinium ions in aqueous solution behave similarly to other large unipositive ions. Their salts with anions of common mineral acids are all very soluble in water and cannot be crystallized; on evaporation of such

(1) (a) G. Wilkinson, *THIS JOURNAL*, **74**, 6148 (1952); (b) E. O. Fischer and W. Pfab, *Z. Naturforschung*, **7B**, 377 (1952); E. O. Fischer and R. Jira, *ibid.*, **8B**, 1 (1953).

(2) Made and reported independently by F. P. Dwyer and A. M. Sargeson, *THIS JOURNAL*, **75**, 984 (1953).

solutions yellow, glassy melts result, and some decomposition occurs. These ions differ somewhat from the cobalticinium ion in being more difficult to precipitate from aqueous solution, even with very large anions. The following reagents, many of which precipitate the cobalticinium ion,¹ failed to precipitate the rhodicinium or iridicinium ions from solutions 1.0 to 10.0 mM in concentration: H_2PtCl_6 , $K_2Co(NO_2)_6$, $KMnO_4$, $KClO_4$, picric acid, salicylic acid, potassium phthalimide, and various substituted naphthol sulfonic acids.

Polyiodides of both ions are obtained upon adding to solutions of at least 0.1 mM concentration a solution of iodide in sodium iodide. However, in contrast to the behavior of the cobalticinium ion with this reagent, no simple triiodides are obtained. Analyses on various samples indicated between five and seven iodine atoms per metal atom.

The addition of bromine water to solutions of at least one mM concentration produces flocculent orange precipitates. If these precipitates are then alternately washed with water and dried in a vacuum desiccator at room temperature, two or three times, pure salts of the tribromide ion Br_3^- result. *Anal.* Calcd. for $(C_5H_5)_2RhBr_3$: C, 25.40; H, 2.18; Br, 51.79. Found: C, 25.46; H, 2.18; Br, 50.68.

Reinecke's salt, $NH_4[Cr(CNS)_4(NH_3)_2] \cdot H_2O$, precipitates the rhodicinium and iridicinium ions from solutions of concentration 0.1 mM or higher. The resulting salts cannot be recrystallized from water because of the instability of the anion. They can be obtained in a quite pure state, however, by digesting them with water below 60° for several hours. *Anal.* Calcd. for $[(C_5H_5)_2Rh][Cr(CNS)_4(NH_3)_2] \cdot H_2O$: C, 29.52; H, 3.19; N, 14.76; S, 22.52; Rh, 18.1; Cr, 9.13. Found: C, 30.19; H, 3.23; N, 14.14; S, 22.81; Rh, 18.9; Cr, 9.16. Calcd. for $[(C_5H_5)_2Ir][Cr(CNS)_4(NH_3)_2] \cdot H_2O$: Cr, 7.74. Found: Cr, 7.93.

With a freshly prepared solution of dipicrylamine, the rhodicinium and iridicinium ions give scarlet precipitates which were recrystallized from acetone.

Anal. Calcd. for $[(C_5H_5)_2Rh][N(C_6H_5N_2O_2)_2]$: C, 39.35; H, 2.10; N, 14.61; Rh, 15.32. Found: C, 39.36; H, 2.06; N, 14.36; Rh, 15.87. Calcd. for $[(C_5H_5)_2Ir][N(C_6H_5N_2O_2)_2]$: C, 34.70; H, 1.85; N, 12.88. Found: C, 33.98; H, 1.94; N, 12.70.

Silicotungstic acid gives precipitates with acid solutions one mM or more in rhodicinium or iridicinium ions.

Solutions of the rhodicinium and iridicinium ions were treated with various oxidizing agents and in no case was there any evidence that they could be oxidized to cations of higher charge. The conclusion that no such higher oxidation states exist is corroborated by the absence of any polarographic oxidation waves in the region 0.0 to +0.5 v. versus S.C.E. The polarograms were made using neutral perchlorate solutions of the ions, concentration about millimolar, with 0.1 M sodium perchlorate as supporting electrolyte.

Polarographic study of a rhodicinium perchlorate solution in a 0.1 M sodium perchlorate supporting electrolyte at pH about 7 (also containing 0.05% gelatin to suppress a maximum which otherwise appeared) shows a cathodic wave at the dropping mercury electrode with a half-wave potential of -1.53 v. versus the S.C.E. Using the polarographic constant for the cobalticinium ion,³ calculation shows that this wave represents a one-electron change, thus corresponding to the reduction of the rhodicinium ion to the neutral bis-cyclopentadienylrhodium(II) compound $(C_5H_5)_2Rh$. Like the neutral compound of cobalt(II), evidence for the existence of which has been obtained in the form of unstable easily oxidized solutions in organic solvents from the reaction of cobalt(II) acetylacetonate with cyclopentadienylmagnesium bromide,⁴ the neutral compound $(C_5H_5)_2Rh$ cannot be isolated from aqueous solutions.

No reduction wave could be obtained for the iridicinium ion since even at a pH of 11 it is masked by a catalytic hydrogen wave. Solutions of Ir^{+3} and Ir^{+4} compounds are known to catalyze the reduction of hydrogen ion at the dropping mercury electrode, and in the present case the effect is probably due to similar action of the reduction or decomposition products formed from the iridicinium ion at the dropping mercury electrode.

Rhodicinium hydroxide was made in aqueous solution by the action of freshly prepared silver oxide on a solution of

rhodicinium chloride. This solution was then titrated potentiometrically with 0.03 N hydrochloric acid using a Beckman Model G pH meter with glass and saturated calomel electrodes. From titration curves so obtained, the value of the dissociation constant of rhodicinium hydroxide was calculated to be 1.1×10^{-3} . Iridicinium hydroxide is a base of comparable magnitude.

The ultraviolet absorption spectra of the rhodicinium and iridicinium ions are shown in Fig. 1 together with the spectrum of the cobalticinium ion. Measurements at several wave lengths indicated that Beer's law is obeyed by solutions of both ions over a concentration range of 0.01 to 1.0 mM.

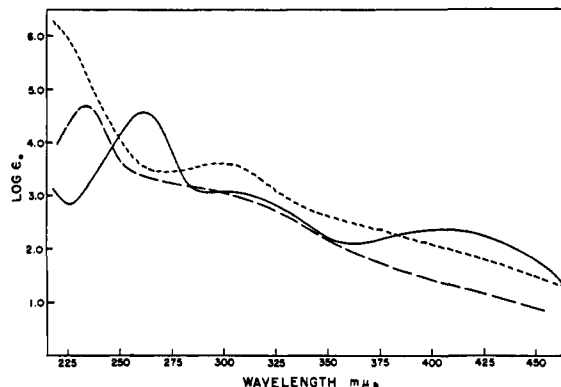


Fig. 1.—Ultraviolet absorption spectra of cobalticinium (—), rhodicinium (---) and iridicinium (— · —) perchlorates in water; Beckman spectrophotometer, silica cells, 25°.

The magnetic susceptibility of rhodicinium tribromide was measured by the Gouy split tube method, using air ($\kappa = +0.029 \times 10^{-6}$ c.g.s.u.) and water (-0.72×10^{-6} c.g.s.u.) as references. The values obtained were independent of field strength. The averaged value of the molar susceptibility, χ_{mol}^{25} , is $-165 \pm 10 \times 10^{-6}$ c.g.s.u.

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Acetic Oxalic Anhydride¹

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The moderate stabilities of the mixed anhydrides of oxalic acid and certain nitrobenzoic acids,³ and of formic acetic anhydride,⁴ together with the chemical behavior of the last-named, suggested that acetic oxalic anhydride (I) might be prepared and might prove useful for the synthesis of oxalic acid derivatives. Furthermore, we wished to ascertain whether it would form amides and esters of acetic acid or of oxalic acid. As its structure is in some ways unique, such preference would be of theoretical interest.

(1) Presented before the 8th Southwest Regional Meeting of the American Chemical Society, Little Rock, Arkansas, December 4-6, 1952.

(2) From Part 1 of the Ph.D. thesis of Walter M. Henley, Louisiana State University, August, 1952.

(3) R. Adams, W. V. Wirth and H. E. French, *THIS JOURNAL*, **40**, 424 (1918); R. Adams and L. H. Ulrich, *ibid.*, **42**, 599 (1920).

(4) A. Behal, *Compt. rend.*, **128**, 1460 (1899).

(3) J. A. Page and G. Wilkinson, *THIS JOURNAL*, **74**, 6149 (1952).

(4) P. L. Pauson, private communication.