As the acid content is increased, the visible peak begins to shift toward that of iodine vapor (520 mμ), a shift which becomes more marked in the region of concentrated acid (see Table I). Note that the molar extinction coefficient is fairly constant, varying by no more than 30% over the entire range.

TABLE I

Concn. of acid, wt. %	$\lambda_{max.}$	$\epsilon_{max.}$
0	460	1.73
11.5	453	1.95
21.9	460	1.56
33.4	465	1.49
38.9	468	1.73
55.5	474	1.43
70.2	481	1.80
79.6	482	1.88
86.5	483	1.78
90.5	493	1.88
94.9	500	2.11

Discussion

The color changes corresponding to the shift of $\lambda_{max.}$ in the visible region may be considered, in terms of the Lewis theory, as arising from two related effects. In the first place, iodine and sulfuric acid are both Lewis acids; consequently, one would expect no electron exchange interaction to occur when these are mixed. In addition, since H_2SO_4 is a stronger acid than I_2 it may displace the halogen from its complex with water. Thus as the acid concentration increases, the color of the solution shifts toward the violet color which one would expect to find in an inert solvent. In the most concentrated sulfuric acid, the visible peak appears at 500 mμ[15] while in typical inert solvents the maximum usually occurs between 510 and 520 mμ. Table II gives values of $\lambda_{max.}$ and molar extinction coefficients, $\epsilon_{max.}$, for iodine in various solvents.

TABLE II

	$\lambda_{max.}$	$\epsilon_{max.}$
Iodine vapor[16]	520	820
n-Heptane[2]	520	910
Carbon disulfide[2]	518	1120
Carbon tetrachloride[2]	517	930
Benzene[2]	500	1040
Mesitylene[2]	490	1185
Diethyl ether[2]	462	880
Water	460	700
Acetone[2]	363	610

Thus the absorption of iodine in concentrated sulfuric acid would lead one to believe that if a complex does exist between iodine and sulfuric acid, it is a relatively weak one.

In general, one might expect sulfuric acid to be an even poorer solvent for non-polar non-electrolytes than water, but any difference is magnified by the fact that the solubility of iodine in water is enhanced by the acid–base interaction which is absent in sulfuric acid. Such an interpretation would account for the steady decrease in solubility from that found in water to that in 80% sulfuric acid; however, the sharp increase in solubility and the high absorption peaks in the ultraviolet observed beyond 90% sulfuric acid do not fit into this picture, and must be due to some as yet unexplained special effect.

NOTE ADDED IN PROOF.—Professor T. F. Young has pointed out to us that our minimum solubility occurs just short of 50 mole per cent. sulfuric acid (84.2% by weight) where he has found the species in solution to be almost exclusively H_3O^+ ond HSO_4^- [*Record Chem. Progress* (*Kresge-Hooker Sci. Lib.*), 12, 81 (1951)]. At higher concentrations, the amount of undissociated sulfuric acid becomes appreciable, which may account for the increased solubility.

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Cyanoethylation of Isophorone

BY HERMAN A. BRUSON AND THOMAS W. RIENER

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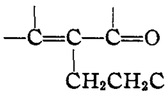
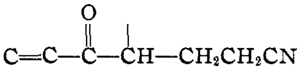
Some time ago it was reported that isophorone resisted cyanoethylation with acrylonitrile.[1] Upon repeating this work with isophorone which had been freed from acidic impurities that poison the alkaline catalyst used for cyanoethylation, namely, benzyltrimethylammonium hydroxide ("Triton B"), it was found possible to obtain mono-, di- and tricyanoethylation products of isophorone.

Infrared analyses were made of these three compounds (1% in chloroform) with a Beckman IR-2T infrared spectrophotometer. Using sodium chloride cells of 16 mil thickness, and maximum gain, spectrograms were obtained covering the range 5.5 to 8.0 μ. A strong absorption peak was observed for all three compounds as well as for isophorone itself, in the neighborhood of 6 μ, ascribed to the conjugated C=C–C=O grouping. For monocyanoethyl isophorone as well as isophorone, this peak occurs at 6.05 μ; whereas for the dicyanoethyl- and tricyanoethyl isophorones the peak occurs at 5.9 μ. Since the grouping



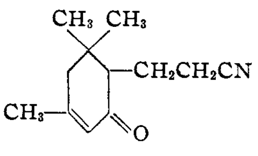
$$-\underset{\substack{|\\ CH_2CH_2CN}}{\overset{|}{C}}=C-\overset{|}{C}=O$$

would be expected to show a greater displacement of the isophorone peak than the grouping



$$C=C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{|}{C}H-CH_2CH_2CN$$

it appears most probable that the monocyanoethylation product has the structure I



I

the dicyanoethylation product the structure II, and the tricyanoethylation product the structure III.

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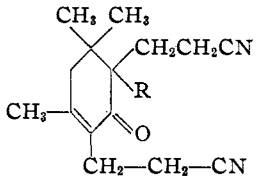
(15) At the American Chemical Society meeting in Atlantic City, New Jersey, on Sept. 15, 1952, R. E. Buckles and J. F. Mills, THIS JOURNAL, **75**, 552 (1953) reported similar observations on the spectrum of iodine in 96% sulfuric acid and drew essentially the same conclusions which we had drawn from our own research, which was then largely complete.

(16) E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 540 (1936).

(1) H. A. Bruson and T. W. Riener, THIS JOURNAL, **64**, 2853 (1942).



II, R = H
III, R = —CH_2CH_2CN

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 oxide[2] 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 $C_{12}H_{17}NO$: 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 $C_{15}H_{20}N_2O$: 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 $C_{18}H_{23}N_3O$: 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. 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 $C_{12}H_{18}O_3$: 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 $C_{15}H_{22}O_5$: neut. equiv., 141. Found: neut. equiv., 140.2.

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

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

BY F. A. COTTON, R. O. WHIPPLE AND G. WILKINSON

RECEIVED FEBRUARY 5, 1953

The great stability of the unipositive bis-cyclopentadienylcobalt(III) (cobalticinium) ion[1] 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 acetylacetonate[2] 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

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[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).