[Contribution from the Petroleum Experiment Station, Bureau of Mines]

The Purification and Some Physical Properties of Cycloöctatetraene

By B. H. Eccleston, H. J. Coleman and N. G. Adams

Introduction

A paper by Scott, *et al.*,[1] of this Station, presented the low temperature heat capacity, heat of fusion, heat of vaporization, vapor pressure and entropy of cycloöctatetraene. This paper describes the purification of the sample used in these studies and presents data on the density, refractive index, viscosity, ultraviolet absorption and infrared absorption of the purified cycloöctatetraene.

Purification

The cycloöctatetraene used in this investigation was a composite sample purified from approximately 90 ml. obtained from the General Aniline and Film Co. through the courtesy of Dr. P. G. Stevens, and 60 ml. obtained by Dr. Karl Kammermeyer at the I. G. Farbenindustrie plant at Ludwigshafen, Germany. The latter sample was transmitted to this Bureau through the courtesy of Dr. Julius Alsberg of the Office of Technical Service, U. S. Department of Commerce.

The separate samples of cycloöctatetraene were first distilled at a nitrogen pressure of 17 mm. in a unit consisting of a vacuum-jacketed rectifying section 1 cm. i. d., 120 cm. long, packed with 3-mm. glass helices, sealed directly to the special column head[2] and to the 200-ml. stillpot. Purified decalin was added near the end of each distillation as a "chaser." The refractive index of each fraction and the ultraviolet absorption curves for selected fractions were obtained.

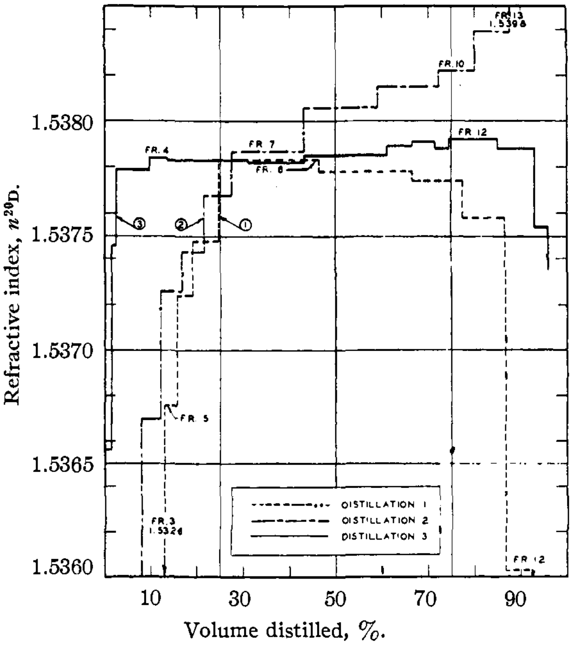

Fig. 1.—Refractive index *vs.* volume per cent. distilled for the three distillations of cycloöctatetraene.

The plot of refractive index, n^{20}D, *vs.* volume per cent. of recovered distillate for the distillation of the sample from the General Aniline and Film Co. (distillation 1) is shown in Fig. 1, curve 1; ultraviolet absorption curves for three of the fractions are shown in Fig. 2. The absorption curve for fraction 12 indicates the presence of a small quantity of styrene, a probable impurity whose absorption curve is also plotted in Fig. 2. The plot of refractive index *vs.* volume per cent. of distillate for the distillation of the sample from the I. G. Farbenindustrie plant (distillation 2) is shown in Fig. 1, curve 2; ultraviolet absorption curves for three of the fractions are shown in Fig. 3. The presence of styrene is much more evident in these fractions than in those of distillation 1. As distillation alone was not an efficient method for removing styrene from the cycloöctatetraene, recourse was made to fractional crystallization. Fractions 4 through 11 of distillation 1 and fractions 3 through 10 of distillation 2 were combined for this work.

Fractional crystallization was conducted in the apparatus shown in Fig. 4, at about −80° in a closed system under an atmosphere of dry nitrogen, as cycloöctatetraene tended to polymerize when exposed to air. The apparatus and method used for the fractional crystallization are new and should be generally applicable to purification of compounds which melt below room temperature and must be protected from air or moisture.

The cycloöctatetraene was introduced into bulb B (Fig. 4), and about one-half transferred by distillation under its own vapor pressure to crystallization vessel A. *n*-Pentane solvent was transferred by distillation under its own vapor pressure from storage bulb C to measuring tube E and thence to crystallization vessel A. The mixture of cycloöctatetraene and pentane was stirred during crystallization by admitting dry nitrogen through stopcock F, through capillary tube to bottom of A, and thence out through stopcock G and mercury bubbler L. A bath of Stoddard solvent around bulb A was cooled slowly by addition of solid carbon dioxide. Crystallization was initiated by removing the bath and holding a piece of solid carbon dioxide against the bottom of the bulb until seed crystals formed. The bath was held at −80° until crystallization was judged to be complete. After removal of the bath mother liquor was drained from crystals by rotating vessel A about the two colinear, spherical, ground-glass joints until it was in a horizontal position (dotted lines in Fig. 5). Mother liquor was forced by nitrogen pressure through platinum filter disk and capillary exit tube into H, thence *via* capillary U-tube J into bulb K. To prevent contact of the mother liquor with lubricated spherical joint, the axis about which vessel A rotated was tilted slightly. As flow of mother liquor through capillary U-tube J was rather slow, bulb H requires capacity enough for volume of liquid drained off at any one time. After draining off mother liquor, nitrogen flow was stopped and capillary U-tube J cooled with liquid air to prevent transfer of material to or from bulb K. After refrigerating bulbs A and K with liquid air and evacuating the system, pentane solvent, measured in tube E, was distilled into bulb A containing cycloöctatetraene from previous crystallizations. (The stopcock above bulb A was turned to by-pass the capillary tube during this operation.) After warming until all cycloöctatetraene was in solution, a second crystallization was conducted as before. Six successive crystallizations were made, each time from fresh solvent. Purified cycloöctatetraene in bulb A (plus occluded solvent from final crystallization) was transferred to bulb D and accumulated mother liquor in bulb K transferred by distillation to bulb M. U-tube J was cooled with liquid air during these operations to prevent transfer of material. The second half of the original crude

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(1) D. W. Scott, M. E. Gross, G. D. Oliver and H. M. Huffman, This Journal, **71**, 1634 (1949).

(2) R. L. Hopkins, *Petroleum Processing*, **4**, 698 (1949).

material was then transferred to bulb A and treated similarly to the first half.

Residual *n*-pentane was removed from the combined product of these two series of fractional crystallizations by distillation at 17 mm. (distillation 3), using the same still but *n*-dodecane instead of decalin for a "chaser." The plot of refractive index *vs.* volume per cent. of distillate for this distillation is shown in Fig. 1, curve 3. Fractions 4 through 12 from distillation 3 were taken as the "best sample." This material, used in obtaining the thermodynamic data[1] and the physical constants and spectroscopic data reported in this paper, was estimated to be 99.9 mole per cent. cycloöctatetraene by a study of the melting point as a function of the fraction melted. The only further treatment of the sample was drying and distilling under its own vapor pressure. When not in use the sample was stored sealed under nitrogen in a cold box.

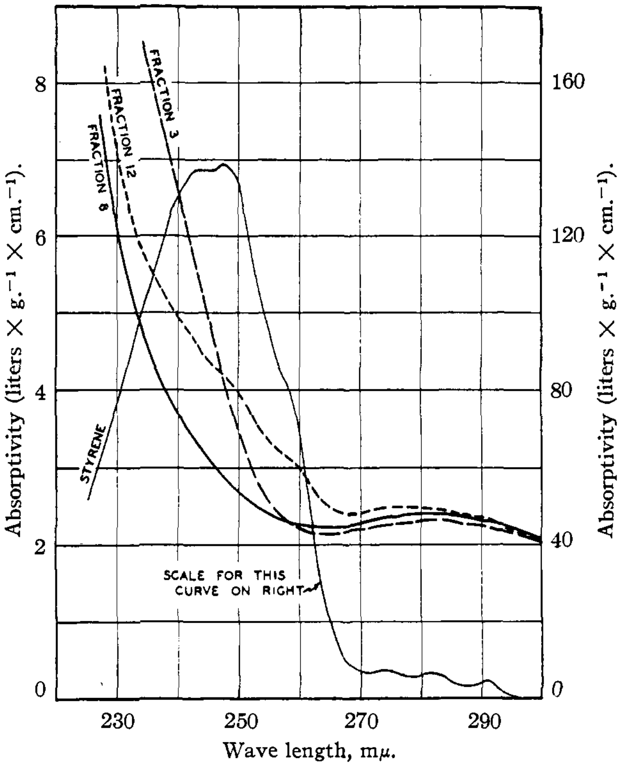

Fig. 2.—Ultraviolet absorption curves for selected fractions from cycloöctatetraene distillation 1, and of a probable impurity, styrene.

Density

The density was obtained in a 5-ml. pycnometer,[3] calibrated at 20, 25 and 30°; baths were controlled to ±0.005°, as indicated by sensitive total-immersion mercury thermometers compared in place with a platinum resistance thermometer in proximity to them in the same bath. The weights were calibrated against a 10-g. weight certified by the National Bureau of Standards. Although the cycloöctatetraene had been stored in an ampoule under nitrogen, the formation of polymer before or during the initial set of density determinations was suspected and confirmed later, as these initial determinations varied from the values in Table I by as much as +0.0002. The cycloöctatetraene therefore, was freed of polymer by a bulb-to-bulb distillation under its own vapor pressure at room temperature, and the density determinations repeated. Two more series of density measurements were made, each time immediately after redistillation of the sample in this manner. These triplicate determinations agreed to the fifth decimal place at 20 and 25° and differed by only two units in the fifth decimal place at 30°. The values obtained are given in Table I.

TABLE I

Temp., °C.	Density, g./ml.
20	0.92094
25	.91963
30	.91172

The results are believed to be accurate to ±0.0001. The equation $d_t = 0.93938 - 0.000922t$ accommodates these data precisely. Some values of density previously reported in the literature are: d^0 0.9382,[4] d^{20} 0.9206,[4] d^0 0.943,[5] d^{20} 0.925.[5]

Viscosity

A Cannon master-type viscometer,[6] calibrated with freshly distilled water, was used to determine the viscosity at 20, 25 and 30°. The bath used was maintained within ±0.01° of the test temperature, as indicated by total-immersion thermometers calibrated against a platinum resistance thermometer. The efflux time was measured with an electric stop clock driven by a 50-cycle, regulated supply. The constants for the viscometer were determined by applying the method of least squares to data for the efflux time for water at the three temperatures, using Bingham's[7] values for the viscosity of water at the various temperatures in calculating the viscometer constants. The data were fitted to the equation $V = Ct - B/t$, where V is the viscosity in centistokes, t the time in seconds, and C and B viscometer constants, 0.0023071 and 0.13353, respectively. The average deviation of the calculated viscosity of water at the three temperatures from the true (Bingham) viscosity was $\pm 1.1 \times 10^{-4}$.

In the initial viscosity determinations, difficulty was encountered because of polymer formation. It was necessary to redistil the sample before each determination at each temperature and to flush the viscometer with nitrogen and keep an inert atmosphere over the ends of the viscometer arms during the determination. Using these precautions, efflux times, for duplicate determinations on different days for each of the temperatures,

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(3) Lipkin, *et al.*, *I. E. C. Anal. Ed.*, **16**, 55 (1944).

(4) Walter Reppe, FIAT 967; see K. Kammermeyer, "Polymerization of Acetylene to Cycloöctatetraene," Field Information Agency Technical (FIAT) final report No. 967 Appendix 5.

(5) Willstätter and Waser, *Ber.*, **44**, 3423 (1911); **46**, 517 (1913).

(6) M. R. Cannon, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 11, 708 (1944).

(7) E. C. Bingham and R. F. Jackson, *Bull. Bur. Stand.*, **14**, 59–86 (SP 298, Aug. 1916).

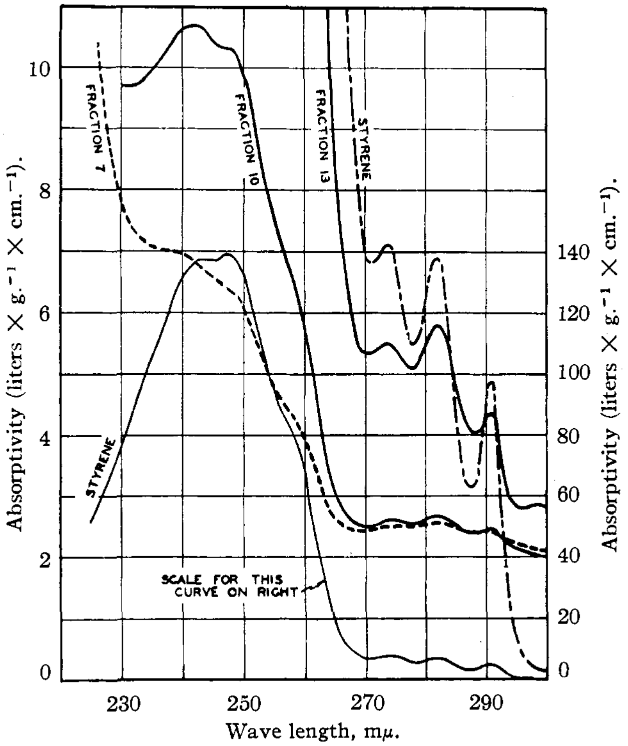

Fig. 3.—Ultraviolet absorption curves for selected fractions from cycloöctatetraene distillation 2, and of a probable impurity, styrene.

were obtained with an average precision of 0.15% or better. The determined viscosity in centistokes, thought to be accurate to within 1%, is presented in Table II.

The relation between the viscosity and temperature, over the range studied, may be expressed by the formula

$$\log_{10} \eta = 673/T - 2.10709 \qquad (1)$$

where η = viscosity in centistokes and T = absolute temperature in °K. The experimental results, in Table II, deviated from those calculated from the equation by a maximum of 1×10^{-3}.

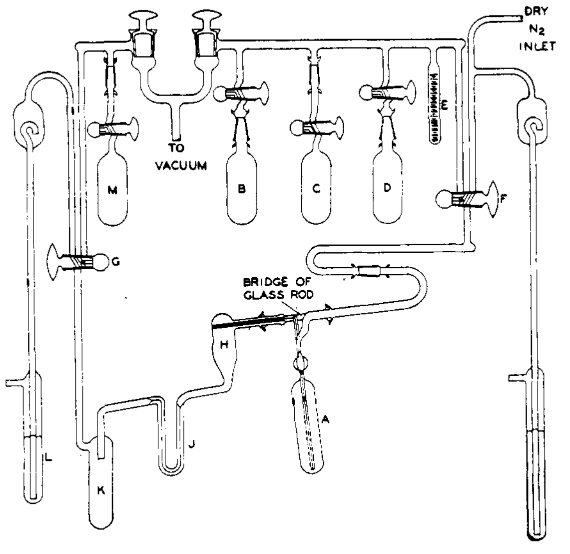

Fig. 4.—The apparatus used for fractional crystallization in a closed system; details of crystallization vessel A are shown in Fig. 5.

Refractive Index

The refractive indices were determined at seven wave lengths by two operators at operating temperatures of 20, 25 and 30°. The instrument (Bausch and Lomb precision refractometer) was set with the glass test piece provided with it, and a calibration curve for each temperature was determined by the use of isoöctane, methylcyclohexane and toluene whose refractive indices for seven wave lengths at the three above temperatures were certified by the National Bureau of Standards. Because of the unavailability of a certified refractive index standard in the cycloöctatetraene range, these curves are extrapolated from the refractive index values of toluene to 1.56 to cover the range of values for cycloöctatetraene.

These calibration curves were applied to the instrument data for cycloöctatetraene, giving the values found in Table III.

These data are thought to be correct within ±0.00010. The compound appears to have strong absorption in the blue end of the spectrum, which causes considerable difficulty in obtaining

Table II

Temp., °C.	Viscosity, cs.	cp.
20	1.5441	1.4220
25	1.4105	1.2971
30	1.2971	1.1826

Table III

Temp., °C.	Wave Length, mμ 667.8 (He)	656.3 (Hc)	589.3 (Na$_D$)	546.1 (Hg$_e$)	501.6 (H$_e$)	486.1 (H$_F$)	435.8 (Hg$_g$)
20	1.53181	1.53260	1.53790	1.54253	1.54885	1.55153	1.56240
25	1.52893	1.52972	1.53501	1.53964	1.54594	1.54866	1.55945
30	1.52632	1.52710	1.53229	1.53693	1.54318	1.54576	1.55663

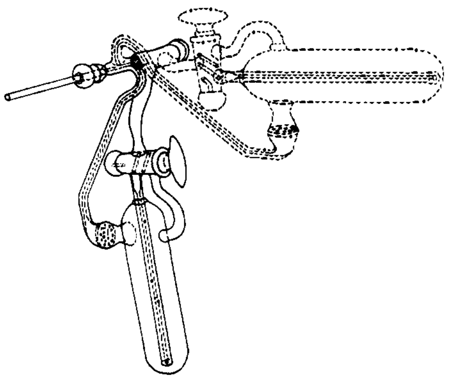

Fig. 5.—The crystallization vessel; see A, Fig. 4.

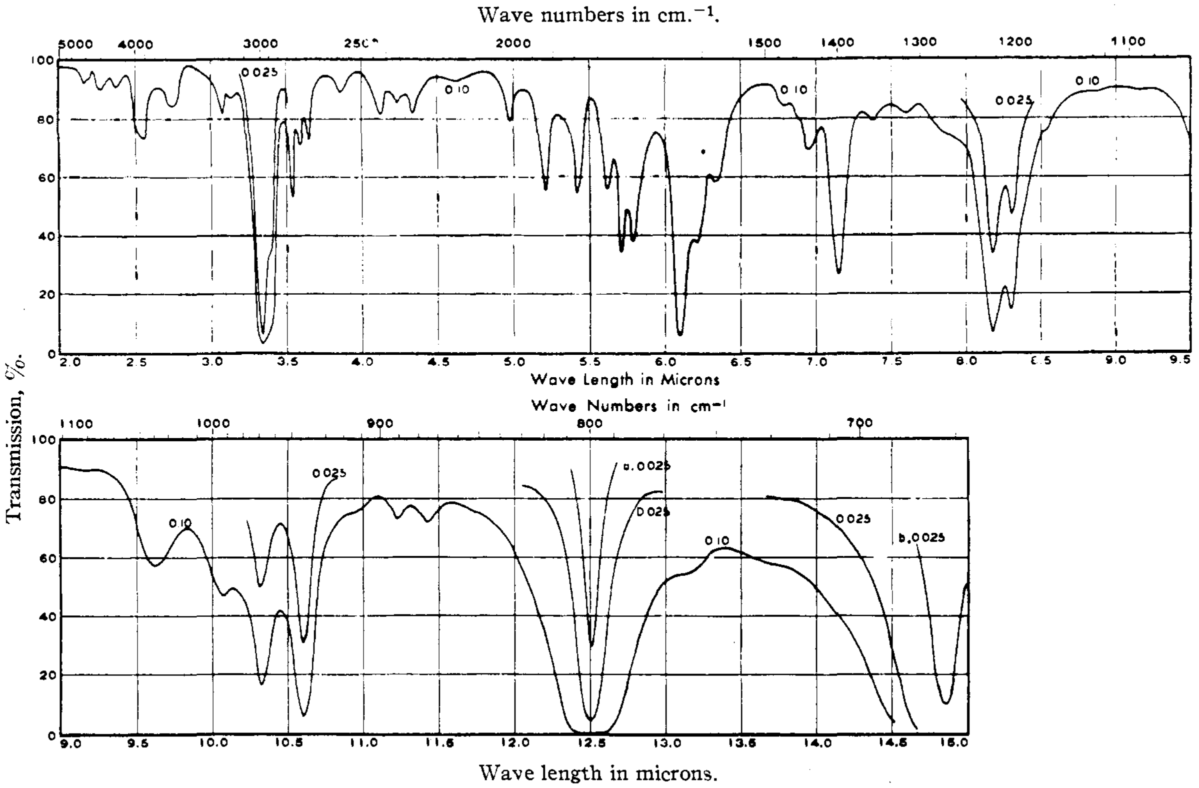

Fig. 6.—Infrared absorption spectrogram of cycloöctatetraene at 25° in the liquid state; cell length is indicated in mm.; a and b represent dilutions of 5% in CS_2 and CCl_4, respectively.

accurate data for the Hg_g line at 435.8 mμ. For this reason the errors in the determinations for this line may exceed the above limits.

The relation between the index of refraction and wave length for cycloöctatetraene may be expressed by a dispersion formula of the Hartmann form.[8,9] Thus the equation

$$n = 1.50997 + 0.008395 \frac{1}{(\lambda - 0.1178)^{1.6}} \qquad (2)$$

appears to express, quite satisfactorily, this relationship at 20° in the wave length range 0.43 to 0.67 micron with each observed value of refractive index fitting the equation within ±0.00006.

Infrared Absorption

The infrared absorption spectrum, Fig. 6, was determined using a Perkin–Elmer model 12-A spectrometer with standard recording equipment as supplied by the manufacturer. A 0.10-mm. cell was used throughout the 2- to 15-micron region, supplemented by one of 0.025-mm. thickness for locating precisely several of the stronger bands. Dilutions to 5% in carbon disulfide and carbon tetrachloride were used in conjunction with the 0.025-mm. cell to locate the maxima of the very strong bands at 12.51 and 14.85 microns, respectively.

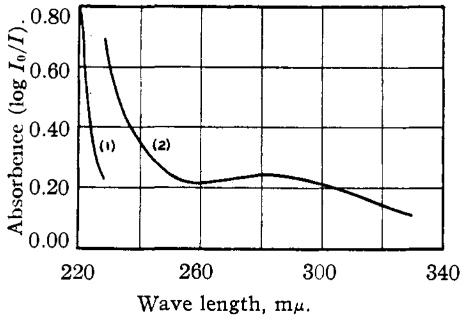

Fig. 7.—Ultraviolet absorption spectrogram of cycloöctatetraene at 25° in solution in isoöctane; (1) and (2) represent concentrations of 0.0298 and 0.0993 g. per liter, respectively, in a 1.00-cm. cell.

Table IV presents the absorption maxima accurate to ±0.01 micron.

The success of the purification process, at least in the elimination of styrene as a contaminant, is indicated by the failure to detect the strong styrene bands near 14.3, 12.9 and 11.0 microns.

Ultraviolet Absorption

The ultraviolet absorption spectrum from 220 to 330 mμ, presented in Fig. 7, was determined on a Beckman model DU photo-electric quartz spectrophotometer. Using isoöctane as a solvent.

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[8] J. Hartmann, *Astrophysics J.*, **8**, 218 (1898).

[9] H. F. Forziati, A. P. I. Research Project 6 Report, May 31, 1949.

TABLE IV

Wave length, μ	Wave length, μ	Wave length, μ	Wave length, μ
2.55	4.12	6.10	9.17
2.75	4.24	6.20	9.63
3.08	4.34	6.32	10.08
3.13	4.63	6.79	10.32
3.34	4.98	6.94	10.60
3.39 s	5.21	7.15	10.95 s
3.54	5.42	7.37	11.23
3.59	5.62	7.59	11.43
3.65	5.71	8.17	12.51
3.86	5.78	8.30	14.85

s, indicates shoulder on side of stronger band.

measurements were taken at two concentrations, 0.0298 and 0.0993 g. per liter, designated (1) and (2), respectively, in the figure. The cells used measured 1.00 cm. in thickness.

Acknowledgments.—The crystallization apparatus described in the foregoing was designed and constructed by D. W. Scott of the Thermodynamics Section of this Station for another purification problem, and only minor modifications were necessary to adapt it for use with cyclooctatetraene.

Summary

The density, viscosity, refractive index and the infrared and ultraviolet absorption spectra of a purified sample of cycloöctatetraene are presented. The purification procedure and the apparatus used are described, and the equations relating to viscosity–temperature, density–temperature and refractive index–wave length over the ranges investigated are given.

BARTLESVILLE, OKLA. RECEIVED DECEMBER 19, 1949

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, COMMERCIAL SOLVENTS CORPORATION]

Hexamminecobalt(III) Benzylpenicillinate[1]

BY ROBERT W. SHORTRIDGE AND CECIL CARR

Recent publications from the University of California College of Pharmacy[2] have indicated that the divalent cobalt ion potentiates the antibacterial activity of penicillin *in vitro* and *in vivo*. It therefore became of some interest to prepare a compound or compounds containing both cobalt and penicillin. Of particular interest were compounds containing various complex ions of trivalent cobalt, from the standpoints of stability and the above-mentioned potentiating effect.

When potassium benzylpenicillinate and hexamminecobalt(III) chloride in a 3:1 molar ratio were dissolved in no more than enough water to make a practically saturated solution of the latter salt, no precipitation occurred. Addition to this solution of a moderate amount of chloroform caused almost immediate formation of an orange-red oil, intermediate in density between the aqueous and the chloroform layer, difficultly soluble in the former, and insoluble in the latter.

Upon continued stirring and rubbing, the oil crystallized, usually within thirty minutes or so, to orange platelets with a pearly luster and showing parallel extinction. These crystals, while insoluble in chloroform, were preferentially wet by it, and in the presence of sufficient chloroform remained suspended therein.

Vapor pressure–composition measurements on the product indicated that it contained chloroform and hexamminecobalt(III) benzylpenicillinate in a 2:1 molar ratio. Its equilibrium vapor pressure in the presence of a little of the chloroform-less salt was 70 mm. at room temperature. It lost chloroform upon drying in air or *in vacuo*, and its elementary composition attained as a limit that of hexamminecobalt(III) benzylpenicillinate trihydrate. Both benzylpenicillinic acid diisopropyl etherate and hexamminecobalt(III) oxalate were prepared in good yield from this product.

A reaction similar to that described above occurs when methylene chloride is substituted for chloroform; an orange-red oil is formed which slowly crystallizes. Upon drying, hexamminecobalt(III) benzylpenicillinate trihydrate is formed.

Hexamminecobalt(III) benzylpenicillinate trihydrate is an orange-red crystalline powder whose melting point is not sharp, but whose decomposition point is around 150°. Its microbiological activity against *Staphylococcus aureus* by the standard cylinder–plate assay approaches closely to the value of 1467 units/mg., calculated from the defined value of 1667 units/mg. for sodium benzylpenicillinate. Any *in vitro* effect of the hexamminecobalt(III) ion on the activity would be reflected in a deviation from the calculated value; therefore, within the limits of accuracy of the test, there is no such effect. *In vivo* tests are being performed and will be reported elsewhere.

The microbiological activity of various samples prepared remained constant during several months' exposure to laboratory conditions, indicating stability of an order comparable to that of the crystalline alkali metal penicillinates.

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(1) This work was presented before the Organic Division at the 116th Meeting of the American Chemical Society at Atlantic City, New Jersey, September, 1949.

(2) (a) Pratt and Dufrenoy, *J. Bact.*, **55**, 727 (1948); (b) Pratt, Dufrenoy and Strait, *ibid.*, **55**, 75 (1948); (c) Pratt and Dufrenoy, *ibid.*, **54**, 719 (1947).