5,7-dihalo-8-quinolinol chelates in absolute ethanol which had been dried over calcium oxide and doubly distilled gave only minor deviations from Beer's law. This is shown by the following data: $Th(C_9H_4Cl_2NO)_4$: 1–5 mg. Th/l., k_{av}[8] at 3420 Å. = 38.7, k_{av} at 3860 Å. = 58.1; $Th(C_9H_4Cl_2NO)_4 \cdot C_9H_4Cl_2NOH$: 1–5 mg. Th/l., k_{av} at 3420 Å. = 49.9, k_{av} at 3860 Å. = 66.1; $Th(C_9H_4Br_2NO)_4$: 2–5 mg. Th/l., k_{av} at 3420 Å. = 41.8, k_{av} at 3880 Å. = 62.0; $Th(C_9H_4Br_2NO)_4 \cdot C_9H_4Br_2NOH$: 1–5 mg. Th/l., k_{av} at 3420 Å. = 56.7, k_{av} at 3880 Å. = 64.6; $Th(C_9H_4ClINO)_4$: 1–5 mg. Th/l., k_{av} at 3460 Å. = 42.1, k_{av} at 3920 Å. = 47.0; $Th(C_9H_4ClINO)_4 \cdot C_9H_4ClINOH$; 1–5 mg. Th/l., k_{av} at 3460 Å. = 53.2, k_{av} at 3920 Å. = 54.2.

The enhanced resistance of ethanol solutions to water is indicated clearly by the typical data for the 1 to 4 dichloro chelate as given in Fig. 2. As much as 10% water by volume has less effect upon ethanol solutions than 0.1% water by volume has upon chloroform solutions. Even though the 5,7-dihalo-8-quinolinol chelates have reduced water sensitivities, they are still sufficiently strongly hydrolyzed to be of doubtful utility for spectrophotometric determinations of thorium.

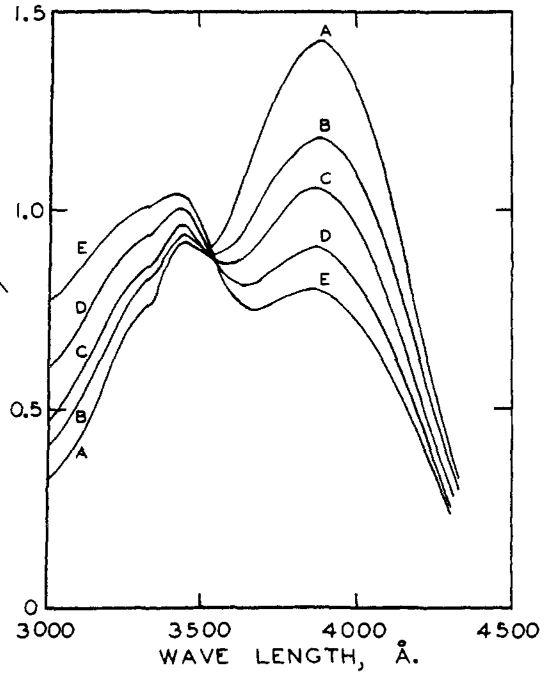

Fig. 2.—Effect of water upon absorption spectra of ethanol solutions of $Th(C_9H_4Cl_2NO)_4$: A, no water; B, 2% water by volume; C, 4% water by volume; D, 12% water by volume; E, 20% water by volume. 5 mg. Th/l. in each case; cell length, 5.0 cm.; temperature, *ca.* 25°.

Acknowledgment.—Funds received from an E. I. du Pont de Nemours and Company Grant-in-Aid for partial support of this investigation are gratefully acknowledged.

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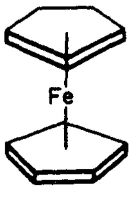
[8] Specific extinction, k, is given by the relationship $k = (\log I_0/I)/cl$, l being in cm. and c being expressed as g. Th/liter.

Bis-indenyl Derivatives of Iron and Cobalt

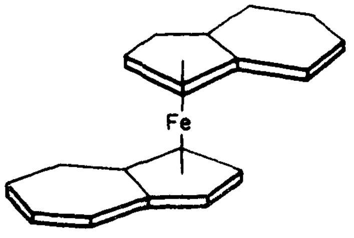
BY P. L. PAUSON AND G. WILKINSON

RECEIVED SEPTEMBER 2, 1953

The discovery of the reaction[1] of cyclopentadienylmagnesium bromide with ferric chloride to yield ferrocene (A) has been followed by the preparation of numerous analogous compounds in which the iron is replaced by other transition metals.[2] In all these cases the cyclopentadiene ring is the characteristic common feature. The present results show that analogous, but somewhat less stable compounds may be derived from indene ("benzocyclopentadiene").



A



B

Thus indenyllithium reacts smoothly with ferric chloride to yield bis-indenyliron(II) or "dibenzferrocene" (B). Figure 1A shows the characteristic infrared spectrum of the deep purple crystals thus obtained. The compound is diamagnetic.

The preparation of the cobalt compound followed the method previously used for the preparation of cobalticinium salts,[3] cobalt(III) acetylacetonate being added to a solution of indenylmagnesium bromide. After decomposing the reaction mixture with ice–hydrochloric acid, salts of the bis-indenylcobalt(III) ion readily can be obtained from the aqueous layer. Like the cobalticinium ion, the "dibenzocobalticinium ion" may be precipitated as the triiodide, tribromide, picrate, reineckate, silicotungstate, etc. The perchlorate is also sparingly soluble in water. Both the picrate and perchlorate have been obtained pure by crystallization from water. Both show remarkably high solubility in polar organic solvents. Figure 1 (B and C) shows the infrared spectra of the perchlorate and triiodide. The strong absorption of the former in the 9μ region is the known absorption of the anion[4]; however, other differences caused by the change of anion, particularly the displacements of the strong peaks at 11.6–11.8 and 13.1–13.3μ appear noteworthy.

On reduction at the dropping mercury electrode, the bis-indenylcobalt(III) perchlorate, in a 0.1 *N* sodium perchlorate supporting electrolyte, shows a well-defined polarographic reduction wave at −0.6 volt *vs.* the standard calomel electrode. The corresponding half-wave potential for cobalticinium perchlorate[5] is −1.16 volt. Thus the annulation of a benzene ring causes a very marked decrease in the reduction potential and conversely

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[1] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

[2] G. Wilkinson, P. L. Pauson and F. A. Cotton, THIS JOURNAL **76**, 1970 (1954), where complete references to earlier work are given

[3] G. Wilkinson, *ibid.*, **74**, 6148 (1952).

[4] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952)

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

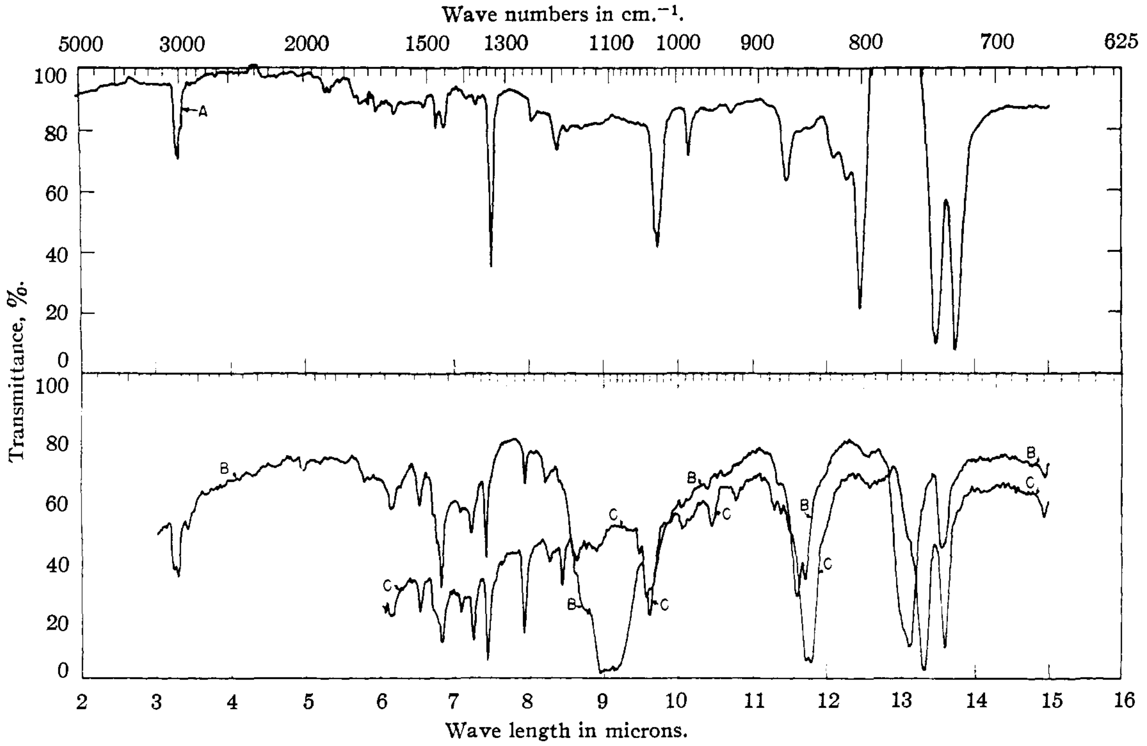

Fig. 1.—A, Infrared spectrum of dibenzferrocene in carbon tetrachloride (2–8μ) and in carbon disulfide (8–15μ); (concn., 20 mg./cc.). Infrared spectra in potassium iodide windows: B, dibenzcobalticinium perchlorate (7 mg.) in KI (1.5 g.); C, dibenzcobalticinium tribromide (14 mg.) in KI (1.5 g.); the change of color observed on grinding the tribromide with the potassium iodide indicates that extensive conversion to the triiodide occurs.

oxidation of the neutral compound to the ion should become more difficult. Attempts to oxidize dibenzferrocene with various oxidizing agents led only to complete destruction of the molecule and no evidence for the formation of a bis-indenyliron(III) ion, analogous to the ferricinium ion[6] was obtained.

Experimental

Bis-indenyliron(II).—To a solution of methyllithium prepared under nitrogen from methyl iodide (48 g.) and lithium (4.8 g.) in ether (500 cc.) is added a solution of indene (33 g.) in benzene (200 cc.). After removal of the ether, the mixture is refluxed until the evolution of methane ceases. It is then cooled in ice and ferric chloride (10 g.) dissolved in ether (200 cc.) is added dropwise over approximately one hour. After complete addition, the temperature is allowed to rise and stirring continued for one hour longer. The resulting mixture is concentrated *in vacuo* to approximately one-half its volume and filtered. From the solid thus obtained, dibenzferrocene may be extracted with hot benzene or ligroin. A further quantity of less pure product may be obtained from the filtrate on further concentration.

Bis-indenyliron(II) is readily soluble in benzene, moderately in acetone, ligroin or ether. It is best crystallized by dissolving in boiling ether and cooling the solution in a Dry Ice–acetone bath. It forms deep purple crystals, density 1.446, m.p. 184–185° (in an evacuated tube), which may be sublimed *in vacuo*.

Anal. Calcd. for $C_{18}H_{14}Fe$: C, 75.6; H, 4.9; Fe, 19.5. Found: C, 75.1; H, 5.0; Fe, 19.6.

The ultraviolet absorption spectrum determined in hexane shows broad maxima at 263 mμ (log ε 4.30) and 420 mμ (log ε 2.78).

The magnetic susceptibility was determined by the Gouy method using the solid, and a value of $\chi_{\text{mol}}^{297°\text{K.}} = -175 \pm 5 + 10^{-6}$ c.g.s.u. was obtained.

Bis-indenylcobalt(III) Salts.—To ethylmagnesium bromide prepared under nitrogen from ethyl bromide (22 g.) and magnesium (4.8 g.) in ether (200 cc.) was added indene (25 g.) diluted with toluene (200 cc.). The ether was removed and the resultant mixture refluxed overnight. After cooling in ice–salt mixture, a solution of cobalt(III) acetylacetonate (8 g.) in benzene (150 cc.) was added dropwise with stirring. Stirring was continued for a further two hours during which the temperature was allowed to rise to room temperature. The product was then poured on a mixture of ice and hydrochloric acid, separated, the organic layer washed with several portions of dilute hydrochloric acid and finally dilute nitric acid. The aqueous solutions thus obtained yielded the characteristic precipitates with reinecke salt and with silicotungstic acid. A portion was treated with saturated aqueous picric acid to precipitate the **picrate**. This is sparingly soluble in benzene, readily in alcohol and in acetone and crystallizes from water in long brown prisms.

Anal. Calcd. for $C_{24}H_{16}N_3O_7CO$: C, 55.7; H, 3.1; N, 8.1; Co, 11.4. Found: C, 56.1, 55.7; H, 3.2, 3.3; N, 7.9; Co, 11.4.

From another portion of the aqueous solution the orange-red **tribromide** was precipitated. Considerable destruction occurred when this was redissolved in hot *N* nitric acid in an attempted purification. The resultant solution was washed with chloroform and the tribromide then reprecipitated. Even after thorough washing and drying this salt retained bromine in excess of the calculated amount as shown by analysis. (*Anal.* Calcd. for $C_{18}H_{14}CoBr_3$. C, 40.9; H, 2.7; Br, 45.3. Found: C, 39.4; H, 2.7; Br, 47.9.) This sample was used for the spectrum shown in Fig. 1C.

The remainder of the material was all precipitated as the dark greenish-grey **triiodide**.

The **perchlorate** was obtained either from the triiodide (after dissolution in hot dilute nitric acid) or from the picrate by passage through an anion-exchange resin in the perchlorate form, but most conveniently by heating the triiodide in 1 *N* perchloric acid with addition of hydrogen peroxide until all the iodine is expelled. The filtered solution then deposits brown prisms of the perchlorate. This is readily soluble in alcohol or acetone and may be recrystallized from hot water.

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[6] G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, THIS JOURNAL, **74**, 2125 (1952).

Anal. Calcd. for $C_{18}H_{14}ClO_4Co$: C, 55.6; H, 3.6; Co, 15.2. Found: C, 55.6; H, 3.8; Co, 15.4.

Acknowledgments.—One of the authors (P. L. P.) is grateful for financial support by the du Pont Company. This work was supported in part by the Atomic Energy Commission.

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The Vapor Pressure of Naphthalene

BY G. W. SEARS AND E. R. HOPKE

RECEIVED JANUARY 19, 1954

Bradley and Cleasby[1] have recently reported vapor pressure data for naphthalene which were found by an effusion method. They obtained a linear log *p* *vs.* $1/T$ plot in disagreement with the measurements of Sears and Hopke,[2] who reported a non-linear log *p* *vs.* $1/T$ curve.

The Sears and Hopke deviation from linearity has been invalidated by the later spectroscopic detection[3] of an impurity, thionaphthene, which was not removed by the purification procedures used. It has been reported independently[4] that commercially pure naphthalene contains about 1% of thionaphthene. The non-linear vapor pressure data were measured with a Rodebush gage, which is quite sensitive to the presence of volatile impurities.

Sears and Hopke[5] have demonstrated the volatile impurity error is minimized by the effusion method of vapor pressure measurement. The purpose of this note is to report later measurements on the vapor pressure of naphthalene by an effusion method which corroborate the data of Bradley and Cleasby.[1]

From 0–20° the data obey a linear log *p* *vs.* $1/T$ relation having the same slope as reported by Bradley and Cleasby. The vapor pressures are 6% lower than those of Bradley and Cleasby. This discrepancy is rationalized in direction and magnitude as no correction was made for the orifice thickness. The orifice thickness was non-uniform and consequently no correction was attempted.

[1] R. S. Bradley and T. G. Cleasby, *J. Chem. Soc.*, 1690 (1953).

[2] G. W. Sears and E. R. Hopke, THIS JOURNAL, **71**, 1632 (1949).

[3] Hertha Sponer, private communication.

[4] W. E. Armstrong, A. B. Densham and G. Gough, *J. Chem. Soc.*, 3359 (1950).

[5] E. R. Hopke and G. W. Sears, *J. Chem. Phys.*, **19**, 1345 (1951).

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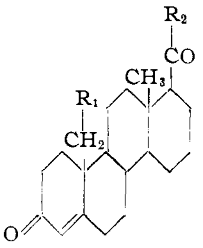
COMMUNICATIONS TO THE EDITOR

19-HYDROXY-11-DESOXYCORTICOSTERONE AND 19-HYDROXYPROGESTERONE[1]

Sir:

One of the aims of work being conducted in this laboratory has been the conversion of the easily accessible cardiac aglycone strophanthidin into analogs of steroid hormones having oxygen in position 19.[2] Recent reports of the isolation from adrenal extracts of electrocortin, a new crystalline hormone having very pronounced sodium-retaining activity, suggest that this product may be an isomer of corticosterone.[3,4] Therefore, we wish to report completion of the synthesis of 19-hydroxy-11-desoxycorticosterone, a new isomer of corticosterone, as well as the two possible monoacetates and the diacetate. We have also prepared 19-hydroxyprogesterone and its acetate.

Successive treatment of the sodium salt of 19-acetoxy-3-oxo-Δ^4-etienic acid (I)[5] with oxalyl chloride and diazomethane produced the non-crystalline 19-acetoxy-21-diazoprogesterone (II).



I, R_1 = Ac; R_2 = OH
II, R_1 = Ac; R_2 = CHN_2
III, R_1 = Ac; R_2 = CH_2OAc
IV, R_1 = Ac; R_2 = CH_2OH
V, R_1 = H ; R_2 = CH_2OH
VI, R_1 = H ; R_2 = CHN_2
VII, R_1 = H ; R_2 = CH_2OAc
VIII, R_1 = H ; R_2 = CH_3
IX, R_1 = Ac; R_2 = CH_3

Heating II with acetic acid gave 19-hydroxy-11-desoxycorticosterone diacetate (III), m.p. 127°, $[\alpha]^{25}\mathrm{D}$ +210°, $\lambda_{\max}^{\mathrm{EtOH}}$ 239 mμ, ϵ 13,400. (*Anal.* Found: C, 70.16; H, 8.12). Hydrolysis of III with potassium bicarbonate yielded 19-acetoxy-11-desoxycorticosterone (IV), m.p. 189–190°, $[\alpha]^{25}\mathrm{D}$ +215°, $\lambda_{\max}^{\mathrm{EtOH}}$ 239 mμ, ϵ 16,000. (*Anal.* Found: C, 71.06; H, 8.65.) Further hydrolysis with potassium carbonate gave 19-hydroxy-11-desoxycorticosterone (V), which melted at 163–165° after a gradual change in appearance over the range 120–145° and sintering at 153–158°, $[\alpha]^{25}\mathrm{D}$ +180°, $\lambda_{\max}^{\mathrm{EtOH}}$ 242 mμ, ϵ 18,500. (*Anal.* Found: C, 72.56; H, 8.70; loss on drying, 2.44.) Hydrolysis of II with potassium bicarbonate gave 19-hydroxy-21-diazoprogesterone (VI), m.p. 166° (*Anal.* Found: C, 70.22; H, 8.21), and reaction of VI with acetic acid produced 19-hydroxy-11-desoxycorticosterone-21-acetate (VII), m.p. 197–199°, $[\alpha]^{24}\mathrm{D}$ +178°, $\lambda_{\max}^{\mathrm{EtOH}}$ 242 mμ, ϵ 13,500. (*Anal.* Found: C, 70.86;

[1] This investigation was supported by a research grant from the National Cancer Institute (Grant No. CG757-C2) of the National Institutes of Health, Public Health Service.

[2] M. Ehrenstein, G. W. Barber and M. W. Gordon, *J. Org. Chem.*, **16**, 349 (1951).

[3] S. A. Simpson, J. F. Tait, A. Wettstein, R. Neher, J. von Euw and T. Reichstein, *Experientia*, **9**, 333 (1953).

[4] V. R. Mattox, H. L. Mason and A. Albert, *Proceedings of the Staff Meetings of the Mayo Clinic*, **28**, 569 (1953); THIS JOURNAL, **75**, 4869 (1953).

[5] P. T. Herzig and M. Ehrenstein, *J. Org. Chem.*, **17**, 713 (1952).