was discharged by the careful addition of ammonium chloride and the reaction was evaporated to dryness under a stream of nitrogen. The solid residue was triturated with 50 ml. of benzene (to remove bibenzyl), then was dissolved in 40 ml. of water. The aqueous solution was treated with Norit, then acidified with acetic acid to cause the precipitation of product (III). Filtration gave 1.53 g. (82%) of colorless product, m.p. 255–256° dec. (uncor.), which was identical in all respects with authentic spongoadenosine (III).[3]

In a larger run, 13 g. of II gave 6.1 g. (94%) of product III, m.p. 254–256° dec.[10]

Pinacol and Pinacolone Derivatives of Some Acylferrocenes

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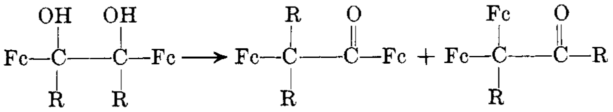
Several examples of the bimolecular reduction of ferrocenyl ketones have been reported in the literature.[1] Weliky and Gould, using methylmagnesium bromide and cobaltous chloride, obtained the pinacol derivative of benzoylferrocene and effected its conversion to the pinacolone. From the Clemmensen reduction of acetylferrocene, Pauson and Watts isolated an 87% yield of ethylferrocene and a 3% yield of the pinacolone derivative.

We wish to report bimolecular reduction of several alkylferrocenyl ketones to the corresponding vicinal diols and subsequent conversion of the diols to the rearranged diferrocenyl ketones. Yields of the diferrocenyl pinacols were 31 to 60% and of the diferrocenyl pinacolones 42 to 60%.

Acetylferrocene failed to undergo the two-step reaction described herein to the pinacolone derivative. However, *n*-propionyl-, *n*-butyryl-, and *n*-valerylferrocene all underwent bimolecular reduction in the presence of amalgamated magnesium to give the corresponding pinacol. With the exception of the bimolecular reduction product of *n*-propionylferrocene, which formed as a monohydrate, the diols were unstable and tended to undergo air oxidation with regeneration of the original ketones.

Rearrangement of the diols could lead to two possible structures for the pinacolones. All of the pinacolones



$$\mathrm{Fc}-\overset{\mathrm{OH}}{\underset{\mathrm{R}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{R}}{\mathrm{C}}}-\mathrm{Fc} \longrightarrow \mathrm{Fc}-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{Fc} + \mathrm{Fc}-\overset{\mathrm{Fc}}{\underset{\mathrm{R}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{R}$$

I II

Fc = ferrocenyl
R = C_2H_5–, *n*-C_3H_7–, *n*-C_4H_9–

were shown to have structure II by virtue of strong carbonyl absorption at 1710 cm.$^{-1}$. All alkylferrocenyl ketones used in this study in which the aromatic moiety is directly attached to the carbon atom of the carbonyl group showed carbonyl absorption at 1675 cm.$^{-1}$ (carbon tetrachloride). No absorption bands at 1675 cm.$^{-1}$ were observed in any spectra of the pinacolones.

The formation of II would be expected with the anticipated migration of the aromatic group rather than the alkyl group during the pinacol–pinacolone rearrangement.[2]

No indications were found of the presence of substances having structure I in any instance. Column chromatography of the pinacolones on Alcoa F-20 activated alumina using 20% benzene in petroleum ether (60–90°) as the eluting agent always gave rise to only one band. The infrared data plus the facts that only one component could be isolated from the pinacolones through column chromatography and that all the pinacolones melted over a narrow temperature range, even before chromatography, tend to indicate that the rearranged ketones are of structure II and are not contaminated with significant amounts of products of structure I.

The pinacolones failed to form either 2,4-dinitrophenylhydrazones or oximes and could not be reduced by either the Clemmensen or Wolff–Kishner reactions. However, confirmatory evidence for the presence of a carbonyl group, in addition to the infrared data, was obtained through the ultraviolet spectra of the pinacolones which showed maximal absorption at 270 mμ.

Experimental[3]

Acylferrocenes.—The liquid ketones were synthesized by the procedure of Vogel[4]; most refractive indices have not been reported hitherto. *n*-Propionylferrocene was obtained as a red oil, b.p. 95–97° (0.1 mm.), $n^{25}\mathrm{D}$ 1.6195 (lit.[5] m.p. 38–39°).

Anal. Calcd. for $C_{13}H_{14}FeO$: C, 64.49; H, 5.83. Found: 64.29; H, 6.11.

n-Butyrylferrocene upon distillation had b.p. 120–122° (0.25 mm.), $n^{25}\mathrm{D}$ 1.6079 [lit.[6] b.p. 144–146° (1.5 mm.), $n^{20}\mathrm{D}$ 1.6073]. *n*-Valerylferrocene upon distillation had b.p. 119–121° (0.08 mm.), $n^{25}\mathrm{D}$ 1.5943 [lit.[7] b.p. 110–120° (air-bath temperature) (0.01 mm.), m.p. 36–38°].

Anal. Calcd. for $C_{15}H_{18}FeO$: C, 66.68; H, 6.71. Found: C, 66.82; H, 7.01.

Preparation of Diferrocenyldiols.—The diferrocenyldiols prepared through bimolecular reduction of the acylferrocenes are listed in Table I. Preparation of 4,5-diferrocenyl-4,5-octanediol (R = *n*-C_3H_7, Table I) exemplifies the general procedure. A solution of *n*-butyrylferrocene (41.8 g., 0.16 mole) and 2.5 g. of mercuric chloride in 75 ml. of dry tetrahydrofuran was added in a slow but steady stream to a boiling mixture of magnesium (2.2 g., 0.09 g.-atom) in 30 ml. of dry benzene. The reaction mixture was heated under reflux with stirring for 36 hr., with protection from atmospheric moisture. The cooled mixture was treated with 15 ml. of water and heated at reflux for 1 hr. Solid was removed by filtration and was extracted with several portions of boiling benzene. The combined filtrates were concentrated *in vacuo*, and the solid residue was washed with petroleum ether (60–90°) until the washings were only faintly yellow. The analytical sample was obtained as brown plates from benzene–

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[10] Private communication from Dr. R. R. Engle, of Riker Laboratories, Inc., Northridge, Calif.

[1] (a) N. Weliky and E. S. Gould, *J. Am. Chem. Soc.*, **79**, 2742 (1957); (b) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 3880 (1962).

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 477.

[3] All melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Model 21 spectrophotometer. The author wishes to thank Messrs. J. E. Sharpe and R. L. Hill for the microanalyses and Mr. R. A. Jewell for the infrared spectra.

[4] M. Vogel, M. Rausch, and H. Rosenburg, *J. Org. Chem.*, **22**, 1016 (1957).

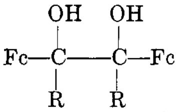
[5] K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *J. Am. Chem. Soc.*, **79**, 3420 (1957).

[6] E. L. DeYoung, *J. Org. Chem.*, **26**, 1312 (1961).

[7] K. Schloegl and H. Pelousek, *Ann.*, **651**, 1 (1962).

TABLE I

DIFERROCENYLDIOLS



$Fc-C(OH)(R)-C(OH)(R)-Fc$

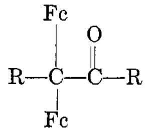
Fc = ferrocenyl

R	Yield, %	M.p., °C.[a]	Calcd., % C	Calcd., % H	Calcd., % Fe	Found, % C	Found, % H	Found, % Fe
C_2H_5-	31	113–115	61.93	6.40	22.15	61.86	6.43	22.30
$n-C_3H_7-$	55[b]	126–128	65.39	6.66	21.72	65.27	6.69	21.93
$n-C_4H_9-$	60[b]	94–97	66.44	7.06	20.60	66.25	7.11	20.85

[a] Recrystallized product. [b] Crude yield.

TABLE II

DIFERROCENYL KETONES



$R-C(Fc)_2-C(=O)-R$

Fc = ferrocenyl

R	Yield, %	M.p., °C.	Calcd., % C	Calcd., % H	Calcd., % Fe	Found, % C	Found, % H	Found, % Fe
C_2H_5-	47	110–111.5	66.70	6.03	23.86	66.67	6.25	23.80
$n-C_3H_7-$	60	108.5–109.5	67.76	6.50	22.51	67.65	6.65	22.55
$n-C_4H_9-$	42	62–64	68.72	6.92	21.31	68.69	7.11	21.33

petroleum ether (60–90°). The infrared spectrum of the diol (tetrachloroethane solution) showed strong hydroxyl absorption at 3400 cm.$^{-1}$. After several days' storage at room temperature, a sample of the solid slowly turned to a reddish brown oil which which was identified through its infrared spectrum as n-butyrylferrocene.

Preparation of Diferrocenyl Ketones.—The rearranged ketones prepared through the dehydration of the diols are listed in Table II. Preparation of 5,5-diferrocenyl-4-octanone ($R = n-C_3H_7$, Table II) illustrates the general procedure. A solution of 4,5-diferrocenyl-4,5-octanediol (10.3 g., 0.02 mole) in 50 ml. of chlorobenzene was added to a solution of 20 ml. of concentrated sulfuric acid in 80 ml. of water. The resulting two-phase system was heated under reflux with vigorous stirring for 6 hr. The organic layer was separated, washed to neutrality with water, and connected *in vacuo*. The residual oil was triturated with methanol and the mixture was allowed to stand at −25° for several hours until solidification was complete. The yellow solid was recrystallized from methanol–benzene as short golden needles. The infrared spectrum of the compound (carbon tetrachloride) showed in addition to the carbonyl band at 1710 cm.$^{-1}$, and other bands, the two absorption bands at 1105 and 995 cm.$^{-1}$ characteristic of mono-ring substitution of ferrocene.[8]

Reduction of acetylferrocene[9] (22 g., 0.1 mole) with magnesium (1.44 g., 0.069 g.-atom) and 1.6 g. of mercuric chloride (50 ml. of tetrahydrofuran and 15 ml. of benzene) as described above gave 18.1 g. of solid with m.p. 146–175°. Even upon temporary storage *in vacuo* it began to decompose to a dark liquid. It was therefore immediately dissolved in 125 ml. of chlorobenzene and added to a solution of 48 ml. of concentrated sulfuric acid in 192 ml. of water. The two-phase system was treated as described above to yield 3.4 g. of solid, m.p. *ca.* 240° dec. The infrared spectrum of the material showed no carbonyl absorption bands at either 1685 or 1715 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{24}Fe_2O$: C, 65.49; H, 5.50; Fe, 25.38. Found: C, 65.73; H, 5.72; Fe, 23.00.

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[8] M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

[9] P. J. Graham, *et al.*, *ibid.*, **79**, 3416 (1957).

The Structure of Alantolactone

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The sesquiterpene lactones alantolactone (I), isoalantolactone (II), and dihydroisoalantolactone (III) were related to eudalene by Ruzicka and co-workers.[1] Subsequently, Tsuda, *et al.*,[2] proved the correct placement of the lactone oxygen and assigned structure IV to alantolactone and structure II to isoalantolactone.

Asselineau and Bory[3] questioned the validity of IV on the grounds that dihydroisoalantolactone (III) and dihydroalantolactone (V)[4] do not give the same chloride with hydrochloric acid.[5] The French workers saponified and oxidized dihydroalantolactone to a keto acid which was isomerized by alkali to a conjugated ketone VI [$\lambda_{\max}^{\mathrm{EtOH}}$ 240 mμ (ϵ 6000)].[3] This evidence supports formulation I for alantolactone.

Recently, Nakazawa[6] obtained identical bromides by hydrobromination of dihydroisoalantolactone and di-

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[1] L. Ruzicka, P. Pieth, T. Reichstein, and L. Ehmann, *Helv. Chim. Acta*, **16**, 268 (1933). These workers favored structure IV (lactone at C-6). The stereochemistry of these compounds has been reviewed by W. Cocker and T. B. H. McMurry, *Tetrahedron*, **8**, 181 (1960).

[2] K. Tsuda, K. Tanabe, I. Iwai, and K. Funakoshi, *J. Am. Chem. Soc.*, **79**, 5721 (1957).

[3] C. Asselineau and S. Bory, *Compt. rend.*, **246**, 1874 (1958).

[4] The configuration at C-11 has recently been proved by W. Cocker and M. A. Nisbet, *J. Chem. Soc.*, 534 (1963).

[5] K. F. W. Hansen [*Chem. Ber.*, **64**, 1904 (1931)] obtained two isomeric hydrochlorides from dihydroisolantolactone. J. Bredt and W. Posth [*Ann.*, **285**, 349 (1895)] prepared the hydrochloride of dihydroalantolactone.

[6] S. Nakazawa, *J. Am. Chem. Soc.*, **82**, 2229 (1960).