borohydride reduction of racemic **1**.[19a] Sodium borohydride (0.91 g, 24 mmol) was stirred in isopropyl alcohol (5 ml) at 0°. Racemic **1** (2.0 g, 18.5 mmol) in isopropyl alcohol (5 ml) was added over a period of 10 min, and the mixture was stirred overnight at room temperature. Water and saturated ammonium chloride were added to decompose excess borohydride. The ether extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated to give an oily residue whose infrared spectrum indicated the absence of a carbonyl band. The residue was purified by Kugelrohr distillation to give 0.42 g (21%) of a white solid, mp 104.5–113° (lit.[19b] mp 109.4–110.8°), which had an infrared spectrum in satisfactory agreement with the reported[19b] spectrum of **5**.

(−)-*endo*-**Dehydronorborneol** (**5**) was prepared from (−)-**1** in a manner analogous to that described above for the racemic compound. The product was purified by distillation (Kugelrohr, 30–50° at 0.005 mm) to give 0.36 g (39%) of a white solid: mp 105–111°; $[\alpha]^{23}D$ −73.4° (*c* 2.62, chloroform). Analysis by glpc on a 2-ft 10% Carbowax 20 M on 60–80 mesh Chromosorb W column at 131° (helium flow 30 cc/min) indicated an *endo/exo* ratio of 91:9; retention time of the *endo* and *exo* isomers were 5.2 and 6.5 min, respectively.

Anal. Calcd for $C_7H_{10}O$: C, 76.31; H, 9.16. Found: C, 75.98; H, 9.05.

Racemic dehydronorborneol was prepared as previously described.[20] The product was a white solid, mp 60–84° (lit.[20] mp 92–93° for racemic *exo*-dehydronorborneol), which was shown to have an *exo/endo* ratio of 87:13 by glpc analysis, as for **5**, above.

Dehydronorbornyl O-Methylmandelate.—Racemic O-methylmandelyl chloride, prepared[11b] from O-methylmandelic acid (1.09 mmol) was stirred magnetically in benzene solution. Pyridine (0.98 g, 12.4 mmol) was added and a precipitate formed. Racemic dehydronorborneol (*exo/endo* ratio 87:13, 0.12 g, 1.09 mmol) in benzene solution was added, and the mixture was stirred at room temperature for 45 min. The work-up was carried out as described for the O-methylmandelamides.[11b] Since impurities were indicated in the nmr spectrum of the crude ester, the product was chromatographed on florisil and eluted with 75:25 v/v benzene–hexane followed by benzene, and 90:10 v/v benzene–ether. The 60-MHz nmr spectrum of the chromatographed material featured a single methoxymethine proton signal at 149 Hz and a single methoxy proton signal at 238 Hz for the mixture of diastereomers from **4**. An analytical sample was collected by glpc (2-ft 10% Carbowax 20M at 210°, helium flow 60 cc/min, retention time 8.2 min).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.05; H, 6.81.

endo-**Dehydronorbornyl O-Methylmandelate.**—Optically pure O-methylmandelyl chloride, prepared[11b] from (−)-(*R*)-O-methylmandelic acid (1 mmol), was treated with pyridine (0.24 g, 3 mmol) and racemic **5** (0.0539 g, 0.49 mmol) as above, for 13 hr at room temperature. The crude ester mixture was chromatographed on florisil, as above. The 60-MHz nmr spectrum of the chromatographed material featured the following signals. The methoxymethine protons in the mixture of diastereomers derived from the *exo* contaminant appeared as a singlet at 149 Hz, and the corresponding protons in the diastereomers derived from **5** appeared at 152.5 and 154.5 Hz. The methoxy protons appeared at 238 (shoulder) and 239 Hz. Electronic integration of the methoxymethine resonances for the diastereomers from **5** in the 100-MHz spectrum indicated a ratio of 1:1. An analytical sample was obtained by distillation (Kugelrohr, 110–115° at 0.02 mm).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.30; H, 7.16.

Determination of the Optical Purity of (−)-*endo*-**Dehydronorborneol** (**5**).—Optically pure O-methylmandelyl chloride, prepared[11b] from (−)-O-methylmandelic acid (1.61 mmol), was treated with pyridine (0.40 g, 5.1 mmol) and (−)-**5** (0.0805 g, 0.71 mmol), $[\alpha]^{23}D$ −73.4° (*c* 2.62, chloroform), as above, for 13 hr at room temperature. The sample used for the nmr measurement was collected by chromatography as described above for racemic dehydronorbornyl O-methylmandelate. The 100-MHz spectrum of the mixture of diastereomers featured the following signals. The methoxymethine protons in the mixture of diastereomers derived from **4** appeared as a singlet at δ 4.63, and the corresponding protons in the diastereomers derived from **5** appeared at 4.59 and 4.55, with that at 4.59 being the more intense. The methoxy protons appeared at δ 3.19 and 3.17. Electronic integration and peak area measurements of expanded scale spectra of the resonances at δ 4.59 and 4.55 indicated that the ratio of diastereomers in the O-methylmandelate derived from (−)-**5**, and hence the ratio of enantiomers in (−)-**5** was 2.65:1.00.

Registry No.—(−)-**1**, 16620-79-4; (−)-*endo*-**5**, 16620-80-7; dehydronorbornyl O-methylmandelate, 16620-82-9; *endo*-dehydronorbornyl O-methylmandelate, 16620-81-8.

(19) (a) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966); (b) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

(20) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

Multinuclear Ferrocenes. V. Allylic Oxidation of 1-Ferrocenylcyclopentene[1]

STANLEY I. GOLDBERG AND ROWLAND L. MATTESON

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Received December 11, 1967

Allylic oxidations of 1-ferrocenylcyclopentene (**3**) by selenium dioxide, chromium trioxide, mercuric acetate, and lead tetraacetate have been studied with the view toward development of a suitable entry into the syntheses of new multinuclear ferrocenes. All oxidations were attended by fairly high degrees of decomposition, and products were obtained in low yields. In all cases oxidation was shown to take place exclusively α to the side of the double bond bearing the ferrocenyl group. Thus, **2-ferrocenyl-2-cyclopenten-1-one** (**5**), **2-ferrocenyl-3-acetoxy-1-cyclopentene** (**7**), and **2-ferrocenyl-3-ethoxy-1-cyclopentene** (**8**) were the oxidation products. While the unsaturated ketone (**5**) underwent unexpected conjugate hydride addition with sodium borohydride to give the saturated alcohol, **2-ferrocenyl-1-cyclopentanol** (**9**); the unsaturated alcohol, **2-ferrocenyl-2-cyclopenten-1-ol** (**6**), obtained from hydrolysis of **7**, was not reduced upon similar treatment with sodium borohydride.

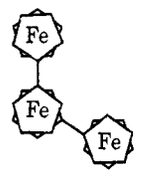
Whereas general methods of synthesis of systems consisting of directly bonded ferrocene nuclei have not been developed to any significant extent, two basic approaches have been used. One, which involves coupling of substituted ferrocenes, has been shown[2] to proceed without rearrangement to substituted biferrocenyls. This approach, however, is attended with serious difficulties at the present time since good general methods of synthesis of a useful range of coupling components is still undeveloped, particularly for appropriately constituted bi- and terferrocenyls.

The second approach lies in the construction of ferrocenylcyclopentadienes, which may then be complexed or "sandwiched" around iron to give the corresponding multinuclear ferrocene systems. The syn-

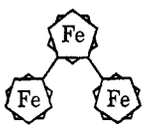
(1) Previous paper in this series: S. I. Goldberg, W. D. Loeble, and T. T. Tidwell, *J. Org. Chem.*, **32**, 4070 (1967).

(2) S. I. Goldberg and R. L. Matteson, *ibid.*, **29**, 323 (1964).

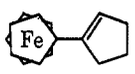
theses of 1,1′-terferrocenyl[3] (1) and 1,2-terferrocenyl[4] (2) provide two examples of that approach; nevertheless, the method is also seriously limited, requiring difficult and numerous steps to achieve the synthesis of a desired cyclopentadiene. Clearly what is needed in this connection is a ready entry into ferrocenylcyclopentadiene systems from which a variety of multinuclear ferrocenes may be obtained. The present study was undertaken to investigate the feasibility of providing such an entry through allylic oxidation of 1-ferrocenylcyclopentene (3).



1

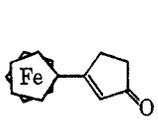


2

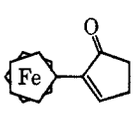


3

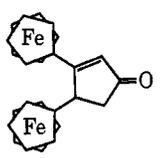
The use of **3** for this purpose appeared to be advantageous, not only for the obvious reason that one ferrocenyl group is directly bonded to a five-membered ring that would become part of a second ferrocenyl group, but also for the practical reason that **3** is obtained in a one-step procedure from ferrocene by treatment of the latter with anhydrous hydrogen fluoride.[5] The question[5,6] of whether the ferrocenylcyclopentene obtained in this way is **3** and/or double bond isomers was easily settled by examination of the nmr spectrum determined from the material. The presence of a low field olefinic proton signal (δ 5.75) which integrated for only one proton clearly showed the structure to be that of the conjugated isomer (**3**).



4



5



10

In principle, allylic oxidation of **3** might be expected to give the two isomeric conjugated ketones, **4** and **5**. These substances could then provide convenient entries into 1,3- and 1,2-disubstituted cyclopentadienes and subsequent conversions into a wide variety of multinuclear ferrocenes. This expectation was not, however, realized experimentally. Oxidation of **3** invariably took place on the more substituted side of the double bond, giving only 3-oxygenated 2-ferrocenyl-1-cyclopentenes. Establishment of this point, which incidentally is in accord with previous observations of relevant allylic oxidations,[7] lay in the chemical correlations made among the various allylic oxidation products obtained during the present study (Table I), and the definitive elucidation of the structure of the ketonic product as that of **5** and not **4**.

(3) K. L. Rinehart, Jr., D. G. Ries, C. H. Park, and P. A. Kittle, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 23C.

(4) S. I. Goldberg and J. G. Breland, Jr., Abstracts, 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, p 308.

(5) V. Weinmayr, *J. Amer. Chem. Soc.*, **77**, 3009 (1955).

(6) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Interscience Publishers, Inc., New York, N. Y., 1965, p 161.

(7) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964).

TABLE I

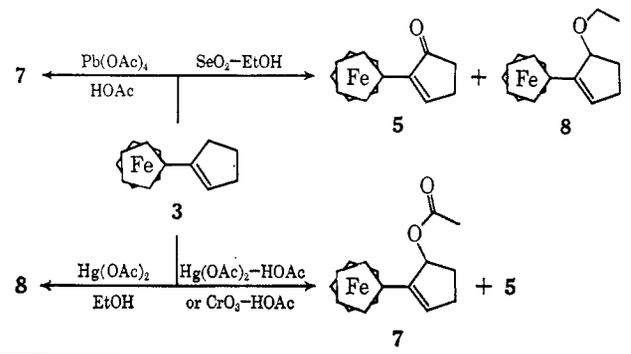
ALLYLIC OXIDATIONS OF 1-FERROCENYLCYCLOPENTENE

Reagent	Reaction time	Temp	Products 3[a]	5[b]	7[b]	8[b]
SeO_2[c]	Overnight	Reflux	4.4	20.3	...	4.4
CrO_3[d]	Overnight	Ambient	7.1	12.9	1.0	...
CrO_3[d]	5 hr	Ambient	25.0	2.7	2.0	...
CrO_3[e]	Overnight	Ambient	35.0	1.5	...	...
$Hg(OAc)_2$[d]	Overnight	Ambient	5.2	4.1	28.1	...
$Hg(OAc)_2$[c]	Overnight	Reflux	16.0	...	...	10.1
$Pb(OAc)_4$[d]	Overnight	Ambient	69.0	...	17.0	...

[a] % recovery. [b] % yield. [c] In 95% aqueous ethanol. [d] In acetic acid. [e] In acetone.

Elementary and spectral analyses of the ketonic product, which was obtained from reaction of **3** with selenium dioxide, chromic anhydride, or mercuric acetate (Table I), was clearly consistent with either structure **4** or structure **5**. The choice in favor of **5** was made by the fact that the chemical shift of the single vinylic proton signal in the nmr spectrum determined from the crystalline substance occurred at δ 7.47. A literature survey of chemical shifts of the α- and β-vinylic protons of conjugated cyclopentenones[8] revealed (20 cases) a range for the α protons to be δ 5.8–6.9 (av = 6.1), while a range of δ 7.2–7.8 (av = 7.6) was found for the β protons. By this criterion the vinylic proton resonance in the nmr spectrum determined from the ketonic product of the present study was attributed to a β proton thus allowing the choice between **4** and **5**.[9] The site of oxygen functions in the acetate (**7**) and the alcohol (**6**) were, therefore, both established by chemical correlation (Scheme II) of these substances with the ketone (**5**). Oppenauer oxidation of **6** gave **5** in 76% yield as the only detectable ketone. The structural relationship of **7** with **5** was established when it was found that hydrolysis of the former gave **6** in 75% yield. While chemical correlation of the remaining oxidation product—the ethoxy compound (**8**)—was not carried out, the site of the oxygen function in this compound was assigned to the same position as in the other oxidation products on the basis of the nmr spectrum obtained from purified compound. Principally, the structural assignment rests on the fact that the chemical shift of

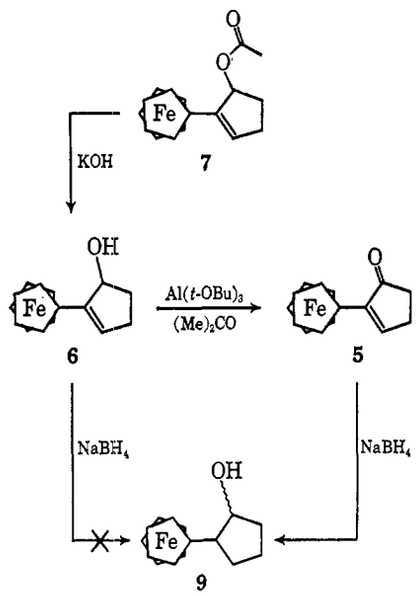
SCHEME I



(8) W. Herz, S. Rajappa, M. V. Lakshmikantham, D. Raulais, and J. J. Schmid, *ibid.*, **32**, 1042 (1967); Y. Inubushi, Y. Sasaki, Y. Tsuda, and J. Nakano, *Tetrahedron Lett.*, 1519 (1965); R. H. Heck, *J. Org. Chem.*, **30**, 2205 (1965); C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *ibid.*, **29**, 3503 (1964); W. Herz, K. Ueda, and S. Inayama, *Tetrahedron*, **19**, 483 (1963); W. G. Dauben, K. Koch, S. L. Smith, and O. L. Chapman, *J. Amer. Chem. Soc.*, **85**, 2616 (1963); and W. Herz, A. Romo de Vivar, J. Romo, and N. Viswanathan, *ibid.*, **85**, 19 (1963).

(9) The value of δ 6.26 for the vinylic proton resonance in **4**, communicated to us by Professor K. L. Rinehart,[3] is well within the range of α proton resonances given above.

SCHEME II



the signal due to the single vinylic proton in the ethoxy compound (δ 5.95) was found to be very close to those in the α,β-unsaturated acetoxy and hydroxy (δ 6.09 and 5.91, respectively) products.

An interesting observation made during this work was the conjugate reduction of the α,β-unsaturated ketone (**5**) to the saturated alcohol (**9**) by the action of sodium borohydride. Since sodium borohydride is generally regarded as a reagent whose use does not lead to conjugate hydride addition in α,β-unsaturated carbonyl systems the present example is noteworthy. Perhaps the explanation lies in the close proximity of the ferrocenyl and carbonyl groups in **5**, providing a favorable situation for coordination of the tetrahydroborate anion which is then able to transfer hydride to the olefinic linkage. Something of this sort is indicated by the facts that neither the isomeric α,β-unsaturated ketone (**4**)[3] nor the diferrocenyl-α,β-unsaturated ketone (**10**)[4] undergo conjugate hydride addition with sodium borohydride, but are each reduced to its corresponding unsaturated alcohol. Finally, failure of the allylic alcohol (**6**) to be reduced by the action of sodium borohydride supports the suggestion that reduction of **5** to **9** involves conjugate addition of hydride to the former.

The results of the present study do not indicate allylic oxidation of **3** to be of great practical synthetic utility for entry into new multinuclear ferrocene systems. All of the reactions are attended by fairly high degrees of decomposition and low yields of products. Of the reactions investigated (Table I), the use of selenium dioxide gave the highest direct conversion to **5**. The use of mercuric acetate or lead tetraacetate gave rise to cleaner reactions and provided the acetoxy compound (**7**) in fair yields. Since **7** was converted to the desired ketone (**5**) in a fairly efficient manner, the best route for synthesis of **5** from **3** appeared to be *via* **7**.

Experimental Section

General.—All temperatures were uncorrected. Melting points were determined in capillary tubes. Preparative column chromatography was used throughout this work to separate reaction products. In each case the Merck acid-washed alumina used was carefully packed, as a hexane slurry, into the column. The material to be chromatographed was then placed (in solution) on the top of the alumina column in a narrow band. Each column was then developed and eluted with appropriate solvents which were previously purified. Infrared spectra were determined with a Perkin-Elmer Model 337 recording spectrophotometer. A Varian Model A-60 nuclear magnetic resonance (nmr) spectrometer was used to record nmr spectra at 60 Mc in chloroform-*d* solution with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm under the δ convention relative to the TMS signal (zero ppm). Electronic spectra were determined with a Perkin-Elmer Model 202 recording spectrophotometer. Combustion analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

1-Ferrocenylcyclopentene (3).—The procedure used here was based on that originally reported by Weinmayer.[5] Ferrocene (10.0 g, 53.8 mmol) was placed into a 100-ml stainless steel reaction vessel,[10] followed by addition of anhydrous liquid hydrogen fluoride (40.0 g, 2.00 mol). The vessel was closed and slowly heated over a period of 8–9 hr to a final temperature of 95° and then allowed to cool slowly to room temperature overnight. After additional cooling of the reaction vessel in an ice bath for 15 min, the vessel was opened and the contents were poured onto crushed ice (1 l.). Several ice–water rinsings were added, and the total hydrolyzate was allowed to warm to room temperature. The mixture deposited a yellow solid, and the initial green color of the supernatant was discharged within 30 min. The desired solid material was collected in a filter (Celite bed) and copiously washed with water. After the contents of the filter were air-dried, the material was placed in a paper extraction and submitted to continuous extraction by benzene in a Soxhlet apparatus until the extracts were colorless. Evaporation of the benzene left a viscous, dark red oil which solidified after about 30 min. Unchanged ferrocene (640 mg) was sublimed [*ca.* 100° (1 mm)], and the sublimation residue was then fractionated under careful distillation conditions. Crude 1-ferrocenylcyclopentene (**3**) was obtained as an orange-colored crystalline solid: 3.89 g (28.9% yield); bp 113–116° (0.35 mm); mp 50–56°. Recrystallization of the product from ethanol gave material which melted at 64–65° (lit.[5] mp 64–65°): infrared $\nu_{max}^{CCl_4}$ 3045, 1640 (trisubstituted, conjugated double bond), 3095 (ferrocene protons), 1105, and 995 cm^{-1} (unsubstituted ferrocene ring); nmr δ^{CDCl_3} 5.75 (1 H, multiplet, vinyl proton), 4.31 (2 H, triplet, α-ferrocenyl protons), 4.14 (2 H, triplet, β-ferrocenyl protons), 4.06 (5 H, singlet, ferrocenyl protons of unsubstituted ring), and 2.7–1.8 (6 H, complex, remaining cyclopentenyl protons); electronic spectrum $\lambda_{max}^{ethanol}$ 210 mμ (ε 23,900), sh 227 (21,000), 276 (9180), and 447 (313) [lit.[5] $\lambda_{max}^{isooctane}$ sh 227 mμ (ε 19,400), 276 (8400), sh 325 (424), and 442 (270).

Several larger runs, using 50–100 g of ferrocene, were carried out[11] in a 3-l. stainless steel vessel[10] in order to accumulate sufficient material.

Properties of Products.—Given below is an account of the physical and spectral properties of the new compounds obtained from the experiments carried out during this investigation.

2-Ferrocenyl-2-cyclopenten-1-one (5) was an orange crystalline solid: mp 83–86°; infrared $\nu_{max}^{CCl_4}$ 3040, 1630 (trisubstituted conjugated double bond), 3095 (ferrocene protons), 1715 (conjugated ketone), 1095 and 1000 cm^{-1} (unsubstituted ferrocene ring); nmr δ^{CDCl_3} 7.47 (center, W = 5 cps, 1 H, multiplet, vinyl proton), 4.74 (2 H, triplet, J = 2 cps, α-ferrocenyl protons), 4.25 (2 H, triplet, J = 2 cps, β-ferrocenyl protons), 4.04 (5 H, singlet, ferrocenyl protons of unsubstituted ring), 2.50 and 2.48 (4 H, singlets, remaining cyclopentenone ring protons); electronic spectrum $\lambda_{max}^{ethanol}$ 212 mμ (ε 16,900), 258 (8040), 285 sh (6470), 382 (412), and 450 sh (300).

Anal. Calcd for $C_{15}H_{14}FeO$: C, 67.70; H, 5.30. Found: C, 68.04; H, 5.57.

2-Ferrocenyl-2-cyclopenten-1-ol (6) was a yellow-orange crystalline solid: mp 105–106°; infrared $\nu_{max}^{CCl_4}$ 3600, 3550, 1045 (hydroxyl group), 3040, 1640 (trisubstituted conjugated double bond), 3095 (ferrocene protons), 1103, and 995 cm^{-1} (unsubstituted ferrocene ring); nmr δ^{CDCl_3} 5.91 (1 H, triplet, J = 2 cps, vinyl proton), 4.97 (center, W = 16 cps, 1 H, unresolved, hydroxyl proton or carbinol proton), 4.47 (2 H, apparent sextet,

(10) American Instrument Co., Inc., Silver Springs, Md.

(11) We wish to acknowledge our thanks to Mr. M. G. Gergel of Columbia Organic Chemicals Co. through whose courtesy arrangements for carrying out these larger runs were made.

α-ferrocenyl protons), 4.23 (2 H, triplet, J = 2 cps, β-ferrocenyl protons), 4.10 (5 H, singlet, ferrocenyl protons of unsubstituted ring), 2.37 and 2.05 (2 H and 2 H, complex, remaining cyclopentenol ring protons); electronic spectrum $\lambda_{max}^{ethanol}$ 210 mμ (ε 22,000), 228 (18,800), 277 (9300), 336 sh (500), and 450 (250).

Anal. Calcd for $C_{15}H_{16}FeO$: C, 67.19; H, 6.01. Found: C, 67.14; H, 5.89.

2-Ferrocenyl-3-ethoxy-1-cyclopentene (8) was yellow-orange oil: infrared ν_{max} 3050, 1640 (trisubstituted, conjugated double bond), 3100 (ferrocene protons), 2950, 2870, 1375, 1120 (ethoxy group), 1100 and 1000 cm^{-1} (unsubstituted ferrocene ring); nmr δ^{CDCl_3} 5.95 (center, W = 6 cps, 1 H, unresolved, vinyl proton), 4.65 (center, W = 8 cps, 1 H, complex, >CH–O), 4.45 (2 H, apparent sextet, α-ferrocenyl protons), 4.18 (2 H, triplet, J = 2 cps, β-ferrocenyl protons), 4.08 (5 H, singlet, ferrocenyl protons of unsubstituted ring), 3.37 (2 H, doublet of quartets, J = 7 and 2 cps, $-O-CH_2-$), 2.33 and 2.10 (2 H and 2 H, complex, remaining cyclopentene ring protons), 1.25 (3 H, triplet, J = 7 cps, $-CH_3$); electronic spectrum $\lambda_{max}^{ethanol}$ 235 mμ (ε 19,500), 273 (34,200), 304 sh (480), and 447 (250).

Anal. Calcd for $C_{17}H_{20}FeO$: C, 68.94; H, 6.81. Found: C, 69.32; H, 6.65.

2-Ferrocenyl-3-acetoxy-1-cyclopentene (7) was a red-orange crystalline solid: mp 86–88°; infrared $\nu_{max}^{CCl_4}$ 3045, 1640 (trisubstituted conjugated double bond), 2960, 2870, 1730, 1470, 1235 (acetoxy group), 3090, 1100, and 1000 cm^{-1} (ferrocenyl group); nmr δ^{CDCl_3} 6.09 (1 H, apparent triplet, J = 2 cps, vinyl proton), 4.31 (5 H, complex α- and β-ferrocenyl protons and >CH–O–), 4.09 (5 H, singlet, ferrocenyl protons of unsubstituted ring); 2.38 (center, W = 9 cps, 4 H, complex, remaining cyclopentene ring protons), 2.10 (3 H, singlet, CH_3CO).

Anal. Calcd for $C_{17}H_{18}FeO_2$: C, 65.83; H, 5.85. Found: C, 65.84; H, 5.97.

2-Ferrocenylcyclopentan-1-ol (9) was yellow crystalline solid: mp 67–68°; infrared $\nu_{max}^{CCl_4}$ 3590, 3500, 1047 (hydroxy group), 3100, 1103, and 998 cm^{-1} (monosubstituted ferrocenyl group); nmr δ^{CDCl_3} 4.13 (10 H, complex, >CH–O and all ferrocenyl protons), 1.78 (center, W = 14 cps, 7 H, unresolved, remain cyclopentanyl protons), and 1.27 (1 H, singlet, hydroxyl protons); electronic spectrum $\lambda_{max}^{ethanol}$ 207 mμ (ε 20,000) and 450 (250).

Anal. Calcd for $C_{15}H_{18}FeO$: C, 66.69; H, 6.72. Found: C, 66.92; H, 6.79.

Allylic Oxidation of 1-Ferrocenylcyclopentene (3). A. Selenium Dioxide in Aqueous Ethanol.—To a solution of 1-ferrocenylcyclopentene (3) (1.00 g, 3.97 mmol) in 30 ml of aqueous ethanol, maintained under gentle reflux and briskly stirred, was added dropwise a solution of selenium dioxide (500 mg, 4.95 mmol) in 25 ml of 95% aqueous ethanol. Reflux heating and stirring was continued overnight (16–18 hr) before the reaction mixture was cooled to room temperature and the precipitated selenium metal separated by filtration. Reduced pressure evaporation of the filtrate to dryness left a residue which was taken up in the minimum volume of methylene chloride and carefully placed onto an alumina column. Development of the column was initially carried out with benzene which eluted unreacted starting material (3); 44 mg, 4.4% recovery. The column was then eluted with a 1:1 (v/v) mixture of benzene and ether which produced a yellow band. Collection and evaporation of that material provided 2-ferrocenyl-3-ethoxy-1-cyclopentene (8); 40 mg, 4.4% yield. The major band of the chromatogram, which was readily eluted with pure ether, yielded the ketone, **2-ferrocenyl-2-cyclopenten-1-one (5)**, 197 mg (20.3% yield).

B. Chromic Anhydride. 1. Acetic Acid Solvent.—To a stirred solution of 1-ferrocenylcyclopentene (3) (2.00 g, 7.94 mmol) in 40 ml of glacial acetic acid was added dropwise a solution of chromic anhydride (1.50 g, 15.0 mmol) in 20 ml of glacial acetic acid containing 2 ml of water. The reaction mixture was kept at room temperature and stirred overnight (16–18 hr). It was then transferred to a separatory funnel, neutralized with aqueous potassium hydroxide solution, and extracted with ether until a colorless ether extract was obtained. After the combined extracts were washed with three small portions of water, they were dried over anhydrous sodium sulfate and evaporated to dryness. The gummy residue which resulted was taken up in the minimum volume of benzene and carefully washed onto the top of an alumina column. Benzene was used to develop and elute two bands of material. From the faster moving band recovered starting material (140 mg, 7.1% recovery) was obtained, while the slower moving band gave 20 mg (1.0% yield) of **2-ferrocenyl-3-acetoxy-1-cyclopentene (7)**. A third band developed with the use of 1:1 (v/v) benzene–ether. It yielded 252 mg (12.9% yield) of **2-ferrocenyl-2-cyclopenten-1-one (5)**.

In another experiment, exactly the same quantities and concentrations of reactants were used. In this case, however, the room temperature reaction was allowed to proceed during only 5 hr. The reaction mixture was worked up as described above, and chromatography again gave the same three substances: starting material 3 (500 mg, 25% recovery), the acetoxy compound 7 (35 mg, 2.0% yield), and the ketone 5 (41 mg, 2.7% yield).

2. Acetone Solvent.—A solution of chromic anhydride (1.00 g, 10.0 mmol) in 25 ml of acetone was added dropwise to a stirred solution of 1-ferrocenylcyclopentene (3) (1.00 g, 3.97 mmol). After the reaction mixture was stirred at room temperature overnight (16–18 hr), it was passed through a filter, and the filtrate was evaporated under reduced pressure. The residue, taken up in the minimum volume of benzene, was chromatographed on alumina. Initial elution with 1:1 (v/v) hexane–benzene gave recovered starting material (350 mg, 35.0% recovery). After changing to pure benzene, two additional bands were developed and eluted. The first (faster) gave **2-ferrocenyl-2-cyclopenten-1-one (5)** (10 mg, 1.5% yield), and the second band yielded a substance (22 mg) which, on the basis of its infrared and nmr spectra, appeared to be an acetone condensation product of the unsaturated ketone (5).

C. Mercuric Acetate. 1. Acetic Acid Solvent.—A solution of mercuric acetate (4.60 g, 14.4 mmol) in 15 ml of glacial acetic acid containing 2 ml of water was allowed to drip into a stirred solution of 1-ferrocenylcyclopentene (3) (4.00 g, 15.9 mmol) at room temperature. The dark-colored solution that resulted was stirred overnight and then passed through a filter to remove the metallic mercury that was deposited. The filtrate was diluted with 250 ml of water and then extracted with ether until a colorless ether extract was obtained. The combined extracts were washed with saturated aqueous sodium carbonate solution until evolution of carbon dioxide was no longer apparent. The ethereal residue was then washed with three portions of water, dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The residue was carefully placed (minimum benzene solutions) onto an alumina column and chromatographed. Starting material (230 mg, 5.2% recovery) was obtained from a hexane–benzene [1:1 (v/v)] eluate. A second band, eluted with pure benzene, gave **2-ferrocenyl-3-acetoxy-1-cyclopentene (7)** (1.27 g, 28.1% yield). Continued elution with benzene produced a third band from which **2-ferrocenyl-2-cyclopenten-1-one (5)** (120 mg, 4.1% yield) was isolated.

2. Aqueous Ethanol Solvent.—A mixture of 1-ferrocenylcyclopentene (3) (2.00 g, 7.94 mmol) and mercuric acetate (2.30 g, 7.22 mmol), dissolved in 60 ml of 20% (v/v) aqueous ethanol, was stirred and heated under gently reflux overnight (16–18 hr). After the reaction mixture had cooled to room temperature, it was diluted with 100 ml of water and then extracted with benzene until a colorless extract was obtained. The oily residual mass, obtained from evaporation of the combined and dried (anhydrous magnesium sulfate) benzene extracts, was dissolved in the minimum volume of benzene and carefully washed onto a column of alumina. Initial elution with 1:1 (v/v) hexane–benzene gave starting material (320 mg, 16.0% recovery). Continued attempts at column development produced only one more band (eluted with benzene) which yielded **2-ferrocenyl-3-ethoxy-1-cyclopentene (8)**; 180 mg, 10.1% yield.

D. Lead Tetraacetate.—A solution of lead tetraacetate (5.50 g, 12.4 mmol) in 25 ml of glacial acetic acid was allowed to drip into a stirred solution of 1-ferrocenylcyclopentene (2.00 g, 7.94 mmol) in 35 ml of glacial acetic acid. After the reaction mixture was stirred at room temperature overnight (16–18 hr) and then diluted with 300 ml of water, it was exhaustively extracted with ether. The combined ether extracts were first washed with saturated aqueous sodium carbonate solution to neutralize the acetic acid and then washed with three portions of water. The ethereal residue was dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to a residue which was dissolved in the minimum volume of benzene and chromatographed on alumina in the usual way. Only starting material (1.38 g, 69.0% recovery) and **2-ferrocenyl-3-acetoxy-1-cyclopentene (7)** (130 mg, 17.0% yield) were obtained [1:1 (v/v) hexane–benzene and pure benzene elution, respectively].

Hydrolysis of 2-Ferrocenyl-3-acetoxy-1-cyclopentene (7) to 2-Ferrocenyl-2-cyclopenten-1-ol (6).—A mixture of potassium

hydroxide (997 mg, 17.8 mmol), the acetoxy compound (7) (1.27 g, 4.10 mmol), and 125 ml of water was stirred and heated on a steam bath overnight. After the reaction mixture had cooled to room temperature, it was exhaustively extracted with ether. Evaporation of the combined and dried (anhydrous magnesium sulfate) ether extracts gave residual material which was placed onto a column of alumina in benzene solution. Elution of the column with benzene gave only a trace of the starting ester. Elution with pure ether provided 820 mg (74.6% yield) of **2 ferrocenyl-2-cyclopenten-1-ol** (6).

Oxidation of 2-Ferrocenyl-2-cyclopenten-1-ol (6) to 2-Ferrocenyl-2-cyclopenten-1-one (5). A. Oppenauer Procedure.—A reaction mixture of 2-ferrocenyl-2-cyclopenten-1-ol (6) (243 mg, 0.907 mmol), aluminum isopropoxide (3.50 g, 17.2 mmol), acetone (10 ml), and toluene (50 ml) was stirred and heated under reflux for 18 hr. After the mixture had cooled to room temperature, it was washed with two portions of 50% aqueous acetic acid and then with three portions of water. The residual toluene solution was dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to a residue which was placed (benzene solution) on an alumina column for chromatographic separation. Development and elution of the column with benzene gave two bands. An odoriferous, yellow oil (130 mg), which was not identified, was obtained from the eluate of the faster moving band. The slower moving band gave 182 mg (75.5% yield) of **2-ferrocenyl-2-cyclopenten-1-one** (5).

B. Activated Manganese Dioxide.—A solution of the alcohol (6) (210 mg, 0.784 mmol) in 50 ml of methylene chloride was stirred overnight at room temperature in the presence of activated manganese dioxide[12] (1.50 g, 17.1 mmol). All of the solid material was then collected in a filter and washed with small portions of methylene chloride until a colorless wash was obtained. The washes were combined with the original filtrate, and the whole was evaporated to a residue which was chromatographed on alumina in the usual way. Elution with benzene gave the ketone (5) (9 mg, 7% yield), while unchanged starting alcohol (6) (70 mg, 30% recovery) was obtained from ether eluates.

Reduction of 2-Ferrocenyl-2-cyclopenten-1-one (5) to 2-Ferrocenyl-1-cyclopentanol (9).—A solution of 2-ferrocenyl-2-cyclopenten-1-one (5) (114 mg, 0.429 mmol) in 25 ml of methanol was stirred and maintained at 0° while sodium borohydride (1.00 g, 26.5 mmol) was added. After addition was complete, the mixture was stirred for an additional 10 min and then diluted with 250 ml of water. The combined ether extracts, obtained from exhaustive extraction of the diluted reaction mixture, were dried and evaporated to a residue which was chromatographed on alumina. Elution with ether gave 73 mg (63% yield) of the saturated alcohol, **2-ferrocenyl-1-cyclopentanol** (9).

Failure of Sodium Borohydride to Effect Reduction of 2-Ferrocenyl-2-cyclopenten-1-ol (6).—Sodium borohydride (67 mg, 1.8 mmol) was added to 25 ml of a cold (0°) methanolic solution of 2-ferrocenyl-2-cyclopenten-1-ol (165 mg, 0.557 mmol) while the latter was stirred vigorously. The stirring was continued for 10 min after the addition was complete, and then the reaction mixture diluted with 250 ml of water. The hydrolyzate was exhaustively extracted with ether, which extracts were combined, dried, and evaporated to yield only unchanged starting material—the unsaturated alcohol (6)—identified by means of its infrared spectrum, 150 mg (91% recovery).

Registry No.—**3**, 12260-67-2; **5**, 12260-661-; **6**, 12260-68-3; **7**, 12260-71-8; **8**, 12260-72-9; **9**, 12260-69-4.

(12) Beacon Chemical Industries, Inc., Cambridge, Mass.

Synthesis of Macrocyclic *o*-Phthalate Esters from the Corresponding Polyesters[1]

WENDELL A. EHRHART

Research and Development Center, Armstrong Cork Company, Lancaster, Pennsylvania 17604

Received August 11, 1967

The esterification of phthalic anhydride with selected glycols in the presence of suitable catalysts (*e.g.*, tetrabutyl *o*-titanate) yields polyesters, from which can be distilled, at 220–260° (0–4 mm), the respective macrocyclic *o*-phthalate esters **1–11**. The *o*-phthalate polyesters of diethylene, triethylene, 1,5-pentylene, and 1,6-hexylene glycols can be converted into the respective macrocycles **1–4** in nearly quantitative yields. Macrocyclic esters **5–11** distill from the corresponding polyesters in relatively poor yields. Saponification of the macrocycles **10a** and **10b** produced the two diastereoisomers of 2-(2-hydroxypropoxy)-1-propanol which have been characterized as their bis-*p*-nitrobenzoates.

Prior to 1930, it was believed that condensations of difunctional compounds always gave rise to cyclic products. Carothers and coworkers[2] established that the condensation of difunctional compounds produces *linear polymers* unless five- or six-membered rings are possible. It was also found, however, that both "monomeric" and higher order macrocycles can often be obtained by thermolysis of these linear polymers *in vacuo*. In fact, cyclic esters of aliphatic dicarboxylic acids, with 11- to 36-membered rings, were obtained in yields of up to 65% by thermolysis of catalyzed polyesters at 270°.[2,3] Small amounts of macrocyclic esters apparently exist in equilibrium with polyester and one another and as one or more of the macrocycles is removed by distillation, more is formed in an attempt to maintain this equilibrium. Although Carothers, *et al.*,[2] suggested that thermolysis of condensation polymers should be a rather general preparative method for macrocycles with practical advantages over high dilution techniques, it appears to have received little subsequent attention.[4–6] The only reference to *o*-phthalate macrocycles is a patent[3] giving melting points of the "monomeric" and "dimeric" macrocyclic ethylene *o*-phthalates (**5** and **6**); however, no other specific information was disclosed. This paper reports on the preparation of *o*-phthalate macrocycles by the polyester thermolysis method.

Polyester Preparation.—Because *o*-phthalic acid is eliminated from carboxy terminated chains as phthalic anhydride, which sublimes and clogs the apparatus, it is expedient to prepare polyesters with acid numbers of less than about five before subjecting them to thermolysis (Chart I).

Although *o*-phthalic acid is relatively difficult to esterify completely, such polyesters have been obtained in 2–6 hr by a melt polymerization technique which employs efficient esterification catalysts, a 20–40% molar excess of the glycol, and precautions to minimize

(1) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(2) W. H. Carothers, *et al.*, in "Collected Papers of Wallace H. Carothers on Polymerization," H. Mark and G. S. Whitby, Ed., Interscience Publishers, Inc., New York, N. Y., 1940.

(3) E. W. Spanagel, U. S. Patent 2,092,031 (1937).

(4) L. I. Belenkii, *Russ. Chem. Rev.*, **33**, 551 (1964).

(5) C. E. Berr, *J. Polym. Sci.*, **15**, 591 (1955).

(6) S. D. Ross, E. R. Coburn, W. A. Leach, and W. B. Robinson, *ibid.*, **13**, 406 (1954).