After 2 hr, solid sodium carbonate was added until all the acid was neutralized, and the mixture was then evaporated to dryness. The residue, treated with 100 ml of water, was extracted with three 50-ml portions of chloroform. The chloroform extracts were washed with water, dried, and warmed to remove all volatile material. The residue was a viscous oil (4.0 g), which could be resolved into two spots (R_f 0.54 and 0.83) on a thin-layer alumina chromatogram with benzene–chloroform (1:1) as the developing solvent. The oil was chromatographed through a 2.2 × 8.6-cm column of neutral alumina prepared from a slurry in benzene–chloroform (1:1). The elution solvents were 50 ml of benzene–chloroform (1:1), 25 ml of benzene–chloroform (1:4), 40 ml of ether–chloroform (1:1), 60 ml of chloroform, and 100 ml of chloroform–methanol. Fractions were monitored by thin-layer chromatography. A clean separation was effected, with the material with R_f 0.53 coming out in the earlier fractions and the material with R_f 0.83 coming out in the later fractions.

The R_f 0.53 material (0.4 g of crystals) was recrystallized three times from chloroform–petroleum ether to give white crystals, mp 124–126°. A mull with mineral oil gave infrared absorption maxima at 3279, 1634, 1538, 1269, and 1242 cm^{-1}. Ultraviolet absorption in the 200–350 mμ region was nil. The sample for analysis, recrystallized further from chloroform–petroleum ether, had mp 125–127°.

Anal. Found: C, 64.44, 64.60; H, 7.00, 7.13; Br, 5.94, 6.19; N, 4.84, 4.65.

The R_f 0.84 material (2.8 g of an oil) was brought out of benzene diluted with ether to give 2.2 g of white crystals XX. Three recrystallizations from acetone–ether furnished material with mp 135–136°.

Anal. Calcd for $C_{15}H_{20}BrNO_3$: C, 52.44; H, 5.97; Br, 23.35. Found: C, 52.38; H, 5.92; Br, 23.42.

A mull in mineral oil gave infrared absorption bands at 3344, 1631, and 1541 cm^{-1}. No ultraviolet absorption was detected between 200–350 mμ. A 3% solution of the borohydride reduction product XX in deuteriochloroform showed nmr signals at 1.7–2.7 (7 H, complex, cyclohexane ring H's), 3.13 (1 H, broad, OH), 3.37 (3 H, s, OCH_3), 4.42 (2 H, d, J = 4 cps, $ArCH_2$), 4.78 (1 H, complex, BrCH), 6.08 (1 H, broad, NH), and 7.27 ppm (5 s, H, ArH's).

Registry No.—IV, 16607-44-6; V, 16607-45-7; VI, 16607-46-8; VIII, 16607-47-9; VIII picrate, 16622-57-4; IX, 16607-48-0; IX 2,4-dinitrophenylhydrazone, 16607-49-1; X, 16607-51-5; X HCl, 16607-50-4; XIV, 16607-52-6; XV, 16607-53-7; XX, 16607-54-8.

Nuclear Magnetic Resonance of 1-Methylimidazole Methiodide. A Correction

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In the course of our studies in imidazoles, we reinvestigated the nmr spectrum of 1-methylimidazole methiodide (**1**), which had been reported in 1965.[1] In contrast to the earlier paper, we have now found that the aromatic protons at C-4 and C-5 absorb at a lower field (H-2, τ 1, 22 ppm, s, broad; H-4,5, τ 2.47 ppm, d, J = 1.7 Hz; in water, DSS = 10) than in 1-methylimidazole itself (2.59, 3.14, and 2.95 ppm; in $CDCl_3$, TMS = 10).[2] The chemical shifts of the corresponding protons in pilocarpine methiodide (τ 1.27 and 2.55 ppm in water) are of the same order. These data are in accord with a report of Mannschreck, *et al.*,[3] that the aromatic protons of imidazole are shifted downfield when the nitrogen is protonated in strong acids. Further we succeeded in splitting the N-methyl signal of **1** into a doublet with $J_{NCH_3,H\text{-}2}$ = 0.45 Hz as anticipated by Mannschreck.[3] The coupling between the N-methyl group and H-2 was confirmed by double resonance.

Registry No.—**1**, 16727-92-7.

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Ozonations of Olefinic Ferrocenes[1]

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The relative ease with which ferrocene may be oxidized presents serious difficulties in projected oxidative transformations of ferrocene derivatives. Thus, for example, in our laboratory we have tried a number of well-established procedures for carbon–carbon double-bond cleavage only to find that destruction of the ferrocene nucleus also occurred. In this Note, we report the results of our study on the ozonation of a series of model olefinic ferrocenes.

Our successful ozonation technique lay in the careful treatment of the olefinic ferrocene with the exact molar equivalent of ozone required for reaction with the alkenyl linkage. For this purpose preparation and use of standardized solutions of ozone in anhydrous ether was found to be satisfactory.

With the monosubstituted olefin, vinylferrocene (**1**), ozonization proceeded smoothly, giving hydroxymethylferrocene (**2**) in 74% yield upon reduction with lithium aluminum hydride. Hydrolysis in the presence of zinc dust provided ferrocenecarboxaldehyde (**3**) in 32% yield, while use of the trimethyl phosphite work-up procedure gave the aldehyde in 85% yield. Three examples of disubstituted olefinic ferrocenes were investigated. Lithium aluminum hydride treatment of the ozonization mixture obtained from 1-ferrocenyl-1-phenylethene (**4**) gave ferrocenylphenylcarbinol (**5**) in 51% yield. Benzoylferrocene (**6**) was produced by hydrolysis and by reaction with trimethyl phosphite in yields of 42 and 45%, respectively. Hydride reduction of the mixture obtained from ozonization of cinnamoylferrocene (**7**) gave the new glycol, 1-ferrocenyl-1,2-dihydroxyethane (**8**), in 36% yield, but no ferrocene compound could be detected after the zinc–water treatment

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[1] (a) Taken in part from the dissertation submitted by W. D. L. to the Graduate School, University of South Carolina, May 1967, in partial fulfillment of the requirements for the Master of Science degree. (b) For a previous paper related to the present work, see S. I. Goldberg, W. D. Loeble, and T. T. Tidwell, *J. Org. Chem.*, **32**, 4070 (1967).

1, R = $—CH=CH_2$
4, R = $—C(C_6H_5)=CH_2$
7, R = $—C(O)CH=CHC_6H_5$
9, R = $—CH=CHCH(CH_3)C_{10}H_9Fe$
11, R = $—C=CHCH_2CH_2CH_2$

2, R′ = $—CH_2OH$
3, R′ = $—CH=O$
5, R′ = $—CH(OH)C_6H_5$
6, R′ = $—C(O)C_6H_5$
8, R′ = $—CH(OH)CH_2OH$
10, R′ = $—CH(CH_3)CH_2OH$

of the ozonization mixture. Similarly, ozonization of 1,3-diferrocenyl-1-butene (**9**) followed by reduction with lithium aluminum hydride gave hydroxymethylferrocene (**2**) and 2-ferrocenyl-1-propanol (**10**) in 32% yield.[1b] When 1-ferrocenylcyclopentene (**11**), an example of a trisubstituted olefin, was allowed to react with the appropriate stoichiometric amount of ozone under the conditions developed in this work, destruction of the ferrocene nucleus was evident from the outset of the addition, for the reaction mixture immediately became very dark. The system was worked up through hydride reduction, but no ferrocene compound could be found.

Although the emphasis in the present study was placed on the practical aspects of ozonation of olefinic ferrocenes, certain other observations are worth noting. First of all, if one assumes that successful double bond cleavage (avoidance of destruction of the ferrocene nucleus) is due to a difference of reaction rate of ozone with the olefin linkage and the ferrocene nucleus, one is faced with the fact that in ordinary olefins the rate of reaction with ozone increases with increasing degree of substitution on the double bond.[2,3] Therefore, it is possible that ozone is not the oxidizing species in the present procedure, and that the process is more complicated than usual ozonations, particularly since it is known that ozone reacts readily with ethers,[4] probably initiating a radical process.[4] Alternatively, the difference may lie in the way the initially formed ozonides decompose.[5]

These questions not withstanding, the results of the present study appear to set the limit of applicability of ozonation at disubstituted olefinic ferrocenes. Despite this rather limited scope it may be anticipated that the procedure will be of utility because it does represent the only means available for the direct cleavage of a carbon–carbon double bond in the presence of a ferrocene nucleus.

Experimental Section

General.—All temperature readings were uncorrected. Columns for elution chromatography were prepared with Merck acid-washed alumina as a slurry in hexane. Column development and elution for each separation is described under the appropriate experimental account. Thin layer chromatography was carried out on glass plates coated with silica gel (0.25 mm). The solvent mixture used for development was composed of hexane, ethyl acetate, and xylene in volume ratios of 6:1:1. Infrared and electronic spectra were determined with Perkin-Elmer, Model 337, and Perkin-Elmer, Model 202, recording spectrophotometers, respectively. Determinations of nuclear magnetic resonance (nmr) spectra were carried out near room temperature with a Varian, Model A-60, spectrometer at 60 Mc in chloroform-*d* solvent containing tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported under the δ (ppm) convention (TMS at δ 0 ppm). Ferrocene was used as purchased from the Ethyl Corporation. Ozone was generated with a Welsbach, Model T-23, Ozonator. The series of olefinic ferrocenes used in this ozonolysis study were all known compounds prepared according to the following literature procedures. Vinylferrocene (**1**) was obtained *via* the dehydration[1b] of 1-ferrocenylethanol[6] prepared by reduction of acetylferrocene. Preparation of 1-ferrocenyl-1-phenylethene[7] (**4**) paralleled that of vinylferrocene in that ferrocenylmethylphenylcarbinol, obtained from the addition of methylmagnesium iodide to benzoylferrocene, was subjected to a similar dehydration procedure. Cinnamoylferrocene[8] (**7**) was prepared through the Friedel–Crafts reaction of cinnamoyl chloride with ferrocene. Treatment of ferrocene with anhydrous hydrogen fluoride was the procedure[9] used for the preparation of 1-ferrocenylcyclopentene (**11**).

Treatment of Ferrocene with Ozone.—Ozone was bubbled into a solution of ferrocene (1.0 g, 5.3 mmol) in dry ether (50 ml) during 10 min. While the system was maintained at −78° (Dry Ice–acetone bath). The ferrocene solution turned to dark black in color almost immediately upon introduction of the ozone. Removal of the solvent left a dark oil in which no ferrocene could be detected by sensitive chromatograpic methods.[10] Several other attempts using shorter time durations also resulted in complete destruction of the ferrocene.

Treatment of Vinylferrocene with Ozone. A. Addition of Ozone.—In all cases when ozone was bubbled into a cold (−78°) ethereal solution of vinylferrocene complete destruction of the latter resulted. This result was avoided, however, with the use of standardized ethereal solutions of ozone.

B. Standard Ethereal Solutions of Ozone.—In each of the ozonation experiments described below the calculated stoichiometric amount of ozone or ozone equivalent was brought into reaction with each olefinic ferrocene system. This was most readily accomplished through the use of ethereal solutions of ozone which were prepared and standardized according to the following generalized procedure. Ozone was slowly bubbled into an appropriate volume of anhydrous ether, maintained near −78° by means of an external Dry Ice–acetone bath, until the appearance of an iodine coloration in the potassium iodide solution through which the gas exiting the ether was passed. The ozone concentration was then precisely determined by addition of a measured aliquot of the ether solution to an appropriate volume of 2% aqueous potassium iodide solution, followed by titration with standard sodium thiosulfate solution (starch indicator) of the iodine equivalent formed. Anhydrous ether thus treated at −78° was usually found to b near 2.5×10^{-3} *M* in ozone equivalent.

C. Ozonation of Vinylferrocene.—The stoichiometric amount of ozone, contained in a cold (−70°) ethereal solution was added very slowly (~45 min) to an ethereal solution (20 ml) of vinylferrocene (100 mg, 0.472 mmol) cooled by means of a Dry Ice–acetone bath. The color of the reaction mixture changed from orange to dark brown during the addition. After the addition was complete and the temperature of the mixture was allowed to rise to 0°, it was then added slowly to a stirred suspension of lithium aluminum hydride (60 mg, 1.6 mmol) in 30 ml of dry ether. Stirring was continued during 30 min, followed by destruction of the excess hydride by addition of ethyl acetate. After the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride and exhaustively extracted with ether, evaporation of the combined and dried ether extracts gave hydroxymethylferrocene (**2**): 75 mg, 74% yield. Crystallization from hexane gave golden needles, mp 78–79° (lit.[11] mp 77–78°), that gave rise to infrared and nmr spectra found to be superimposable upon those determined from authentic hydroxymethylferrocene.[12]

In another run vinylferrocene (100 mg, 0.472 mmol) was treated with stoichiometric equivalent of ozone as described above. The cold (−78°) reaction mixture was poured into 75 ml

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of ice–water containing zinc dust (8 g) and stirred while the temperature was allowed to rise to room temperature. Periodic tests[13] showed the absence of peroxide during the hydrolysis. The ethereal phase was separated, and the aqueous phase was extracted with several portions of ether. Evaporation of the combined and dried ether solutions gave dark red crystals which showed only one major spot corresponding to ferrocenecarboxaldehyde on a thin layer chromatogram. The material was column chromatographed [benzene–ether, 1:1 (v/v)] to give 32 mg (32% yield) of pure ferrocenecarboxaldehyde (**3**): mp 124–125° (lit.[14] mp 124.5°); infrared and nmr spectra identical with those obtained from authentic material.

In a third run, trimethyl phosphite (91 mg, 0.73 mmol) was added to the cold (−78°) ozonization mixture of vinylferrocene (100 mg, 0.472 mmol), which was obtained as described above. During the addition the temperature of the reaction mixture rose to −20°, and after the addition was complete the mixture was allowed to come to room temperature. The ethereal solution was washed with several small portions of water, dried, and evaporated to a brown oil which was column chromatographed. Elution with benzene provided ferrocenecarboxaldehyde (**3**), identified by its infrared and nmr spectra (86 mg, 85% yield).

Ozonation of 1-Ferrocenyl-1-phenylethene (4).—1-Ferrocenyl-1-phenylethene (200 mg, 0.694 mmol), dissolved in 20 ml of anhydrous ether and cooled to −78°, was treated with the appropriate amount of standardized ethereal ozone solution in the usual way. During the addition the color changed from deep red to orange, and, after 30 min at −78°, the reaction mixture was allowed to warm to room temperature before it was added to a stirred suspension of lithium aluminum hydride (80 mg, 2.1 mmol) in 100 ml of ether. After the excess hydride was destroyed with ethyl acetate and the mixture hydrolyzed with saturated aqueous ammonium chloride solution, the aqueous phase was separated and extracted with several portions of ether. Evaporation of the combined and dried ether solutions left ferrocenylphenylcarbinol (**5**) [103 mg, 50.9% yield; mp 81–2° (lit.[7] mp 81–82°)] which gave rise to the infrared and nmr spectra superimposable upon those determined from authentic[7] ferrocenylphenylcarbinol.

The cold (−78°) ozonation mixture, prepared in the usual way from 1-ferrocenyl-1-phenylethene, was poured into 100 ml of ice–water containing zinc dust (8.0 g) and stirred for 1 hr, during which time periodic tests[13] for the presence of peroxide were negative. After the separated ether layer was washed with water and dried, it was evaporated to leave a residue of deep red cyrstals which was column chromatographed. Elution with benzene gave rise to pure 84 mg (42% yield) of benzoylferrocene mp 111–112° (lit.[15] mp 111–112°), whose identity was confirmed by comparison of its infrared and nmr spectra with those obtained from authentic benzoylferrocene.

Trimethyl phosphite (114 mg, 0.919 mmol) was added to the cold ozonization mixture prepared from 1-ferrocenyl-1-phenylethene (200 mg, 0.694 mmol), giving an exothermic reaction. The ethereal solution was washed with several small portions of water, dried, and evaporated to a brown oil which was column chromatographed. Elution of the prominent red band with benzene gave 91 mg (45% yield) of benzoylferrocene, mp 111–112°. Both admixture melting with authentic benzoylferrocene and comparison of infrared spectra were used to establish the identity.

Ozonization of Cinnamoylferrocene (7).—An ethereal solution (20 ml) of cinnamoylferrocene (157 mg, 0.497 mmol) was cooled to −78° and treated with an equivalent amount of ozone contained in cold (−78°) ether. The original orange color persisted while the mixture was kept at −78° during 30 min. At that time the cold solution was added to a stirred suspension of lithium aluminum hydride (80 mg, 2.1 mmol) in 100 ml of ether. After 30 min of stirring the excess hydride was destroyed by addition of ethyl acetate, and the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride solution. The ether extracts of the aqueous phase were combined with the original ethereal phase, and the whole was dried and evaporated to give an orange gum which was carefully placed onto a silica gel column. Elution of the major band (orange) gave a substance whose spectral properties were found to be consistent with 1-ferrocenyl-1,2-dihydroxyethane (**8**): 44 mg, 36% yield; ir (CCl_4), 3560 (O-H), 3100 (Fc-H), 2950, 2925 (C-H), 1095 and 1000 cm^{-1} (unsubstituted Fc ring); nmr ($CDCl_3$), δ 4.21 (complex, 12), 3.42 (s, 1) and 1.23 (s, 1).

The cinnamoylferrocene ozonization mixture prepared as described above was poured into a stirred mixture of ice–water and zinc dust. As usual periodic spot tests for the presence of peroxide were negative. However, no ferrocene compounds could be found in the ethereal phase or extracts of the hydrolysate, and only some intractable tar was obtained from the aqueous portion.

Treatment of 1-Ferrocenylcyclopentene (11) with Ozone.—1-Ferrocenylcyclopentene (130 mg, 0.516 mmol) was dissolved in 20 ml of anhydrous ether and cooled at −78° while an equivalent of ozone (0.516 mmol) was slowly added *via* the usual standardized ethereal solution. The reaction mixture became brown-black immediately. After it was allowed to warm to room temperature the dark reaction mixture was added slowly to a stirred suspension of lithium aluminum hydride (60 mg, 1.6 mmol) in 100 ml of ether. The stirring was continued for an additional hour before the excess hydride was destroyed (ethyl acetate) and the mixture was hydrolyzed (saturated ammonium chloride). The only material detected and isolated from the ethereal phase and extracts was the starting compound 1-ferrocenylcyclopentene (13 mg, 10% recovery).

Registry No.—**8**, 12269-77-1.

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The Reaction of Phenylacetylene with Nickel Carbonyl and Lithium Dimethylamide

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It has been known that lithium aroyl, or lithium acyl metal carbonylates $Li[RCOM(CO)_x]$ (R = alkyl or aryl) are formed from the reaction of organolithium compounds with mononuclear metal carbonyls.[1] Previously, it was reported from our laboratory that lithium aroylnickel carbonylate, one of these unstable complexes, gave ketone or α-diketone by thermal decomposition and acyloin by hydrolysis.[1c] Furthermore, as this complex has a carbon–transition metal σ bond, it undergoes reaction with acetylenic compounds very easily to give 1,4-diketones in high yields.[2]

Analogous to the formation of lithium aroylnickel carbonylate, the formation of lithium carbamoylnickel carbonylate (I), $Li[RR'NCONi(CO)_3]$, from the reaction of lithium amide with nickel carbonyl is predicted. In fact, the formation of I ($R = R' = CH_3$) was confirmed by the infrared spectrum of the reaction mixture of lithium dimethylamide and nickel carbonyl. This carbamoyl complex also has a carbon–metal σ bond; so it is expected that the complex undergoes reaction with acetylenic compounds to give succinic acid amide derivatives directly. In the case of lith-

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