steroid but was clearly neither 5α- nor 5β-cholestane.[24] The infrared spectrum indicated the absence of any functional groups such as OH or carbonyl. The molecular weight of the material was 372 by mass spectrometry.

Reduction of *cis,cis,trans*-Perhydro-9b-phenalenol (15) by Hydride Transfer.—Alcohol **15** (1.94 g, 10 mmol) was dissolved in 40 ml of methylene chloride along with 2.99 g (11.5 mmol) of triphenylsilane and 7.3 ml (11.2 mg, 100 mmol) of trifluoroacetic acid. After 48 hr the solution was poured in 250 ml of saturated sodium bicarbonate, the layers separated, and the aqueous layer was extracted with 50 ml of methylene chloride. The combined organic extracts were washed with 50 ml of saturated sodium bicarbonate, dried over magnesium sulfate, concentrated, and chromatographed on 40 g of silica gel (Woelm). Elution with 120 ml of pentane yielded 1.63 g (92%) of **18**. The reaction product was identical with respect to ir, nmr, and retention time (10-ft 15% Carbowax on firebrick at 188°) with an authentic sample. Analysis by glpc under these conditions indicated that the product was 90% pure.

Reaction of 15 with Trifluoroacetic Acid.—To 300 mg (1.55 mmol) of **15** in 10 ml of methylene chloride was added 2.5 ml of trifluoroacetic acid, and the solution was allowed to stand 30 min and then poured into 50 ml of saturated sodium bicarbonate solution. The organic layer was dried over magnesium sulfate and evaporated. Previous experiments had indicated that the product at this point was a trifluoroacetate ester which was difficult to purify directly. For identification purposes the product was taken up in 10 ml of methanol containing 1 g of KOH, allowed to stand 48 hr, then quenched with 50 ml of water, and extracted with four 25-ml portions of pentane. The pentane layers were washed twice with 5-ml portions of water, dried ($MgSO_4$), and evaporated to leave 216 mg (72%) of white solid, mp 81–84°. The infrared spectrum was identical with that of *trans,trans,trans*-perhydrophenalen-3a-ol (**20**). A small amount was recrystallized from pentane to yield material melting at 87.5–88.5°.

Conversion of 2-Methyl-2-adamantanol to 2-Methyladamantane (22).—Trifluoroacetic acid (7.3 ml) was added to a solution of 1.66 g (10 mmol) of 2-methyl-2-adamantanol and 2.0 ml of triethylsilane in 40 ml of methylene chloride. The combined extracts were dried over magnesium sulfate and evaporated, and the residue was recrystallized from ethanol–water to afford 613 mg (41%) of **22** as white crystals, mp 144–146° (reported[25] 143.8–146°). The nmr spectrum of the product provided confirmation of the supposed structure in that it exhibited a three-proton doublet ($J = 7$ Hz) at 1.05 ppm (reported[26] 1.04 ppm).

To check for completeness of the reaction, because of the low yield realized in the preparative experiment and to ensure that no rearrangment of the carbonium ion was occurring under these reaction conditions, 50 mg of 2-methyl-2-adamantanol and 85 mg of Ph_3SiD were dissolved in 0.4 ml of $CDCl_3$ in an nmr tube and 0.075 ml of trifluoroacetic acid was added. After 48 hr at 25° the nmr spectrum of this solution showed that **23** was formed quantitatively. The methyl signal appeared at 1.05 ppm as a broadened singlet which was found to be a triplet on scale expansion due to vicinal coupling of the methyl protons with one deuterium nucleus ($J = 1$ Hz).

Registry No.—**1**, 597-49-9; **4** (cation), 27390-89-2; **5**, 23373-80-0; **12**, 27390-90-5; **16**, 27390-91-6; **20**, 27390-92-7; **21**, 27411-03-6; diethylsilane, 542-91-6; triphenylsilane, 789-25-3; triethylsilane, 617-86-7.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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[24] 5α-Cholestane was purchased from Applied Science Laboratories, State College, Pa. 5β-Cholestane was obtained from Chemical Procurement Laboratories, College Point, N. Y.

[25] P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961).

[26] R. C. Fort, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 785 (1965).

Ferrocene Studies. XVIII. Identification and Stereochemistry of Nine Bimolecular Clemmensen Reduction Products of Benzoylferrocene[1a–d]

STANLEY I. GOLDBERG,* WILLIAM D. BAILEY, AND MARTIN L. MCGREGOR[1e]

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

Received June 10, 1970

In addition to the normal reduction product, benzylferrocene, Clemmensen reduction of benzoylferrocene is shown to give nine bimolecular reduction products: achiral and chiral 1,2-diferrocenyl-1,2-diphenylethanes (**3** and **4**), *trans*-1,2-diferrocenyl-1,2-diphenylethene (**5**), 2,2-diferrocenyl-1,2-diphenylethanone (**6**), 1,2-diferrocenyl-2,2-diphenylethanone (**7**), achiral and chiral 1,2-diferrocenyl-1,2-diphenyl-1,2-ethanediols (**8** and **9**), and achiral and chiral 1,2-diferrocenyl-1,2-diphenylethanols (**10** and **11**). Rigorous stereochemical assignments to the achiral and chiral diastereomers of the ethanes, **3** and **4**, and the diols, **8** and **9**, are based on independent preparations of each pair in the presence of (+)-(*S*)-1-methoxy-2-methylbutane (**12**). These successful procedures of asymmetric selection give an optically active form (chiral) along with an optically inactive partner (achiral) in each case. The olefinic Clemmensen product is shown to consist of only the trans or *E* isomer **5** by its conversion, *via* overall syn addition of hydrogen, to the chiral ethane **4**. Stereochemical assignments to the alcohols, **10** and **11**, are mainly but tentatively based on the relative rates with which these highly unstable compounds undergo fragmentation to benzyl- and benzoylferrocene.

Although the Clemmensen reduction[2] is generally used in the conversion of ketones to $-CH_2-$ groups, bimolecular reduction products are sometimes formed.[3] The present work is concerned with the reduction of benzoylferrocene for which bimolecular products are known to predominate.[4] We have carried out a large

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[1] (a) First part of a subseries concerned with Clemmensen reductions of ferrocenyl ketones. Portions of this work have been presented in preliminary form.[1b–d] (b) 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, Abstracts, p 308. (c) S. I. Goldberg and W. D. Bailey, *J. Amer. Chem. Soc.*, **91**, 5113 (1969). (d) S. I. Goldberg and W. D. Bailey, *J. Chem. Soc. D*, 1059 (1969). (e) A part of the experimental work is from the Ph.D. dissertation of M. L. McGregor, University of South Carolina Graduate School, 1969, and the work contributed by W. D. Bailey is to be included in his Ph.D. dissertation.

[2] E. Clemmensen, *Ber.*, **46**, 1838 (1913).

[3] For accounts of much of this work, see E. L. Martin, *Org. React.*, **1**, 155 (1942); J. H. Brewster, *J. Amer. Chem. Soc.*, **76**, 6361, 6364 (1954); D. Staschewski, *Angew. Chem.*, **71**, 726 (1959); T. Nakabayashi, *J. Amer. Chem. Soc.*, **82**, 3900, 3906, 3909 (1959).

[4] The claim[5] that the unidentified material obtained from Clemmensen reductions of benzoylferrocene (Rausch, Vogel, and Rosenberg[6] and Nesmeyanov and Kritskaya[5]) was 2,2-diferrocenyl-1,2-diphenylethane has been refuted.[7] It is likely that those isolations, as well as the unidentified material reported by Weliky and Gould,[8] consisted of various combinations of the bimolecular products incompletely accounted for earlier[1b,9] but more fully recognized in the present work.

[5] A. N. Nesmeyanov and I. I. Kritskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 352 (1962).

[6] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).

[7] S. I. Goldberg and M. L. McGregor, *ibid.*, **33**, 2568 (1968).

[8] N. Weliky and E. S. Gould, *J. Amer. Chem. Soc.*, **79**, 2742 (1957).

[9] M. D. Rausch and D. L. Adams, *J. Org. Chem.*, **32**, 4144 (1967).

SCHEME I

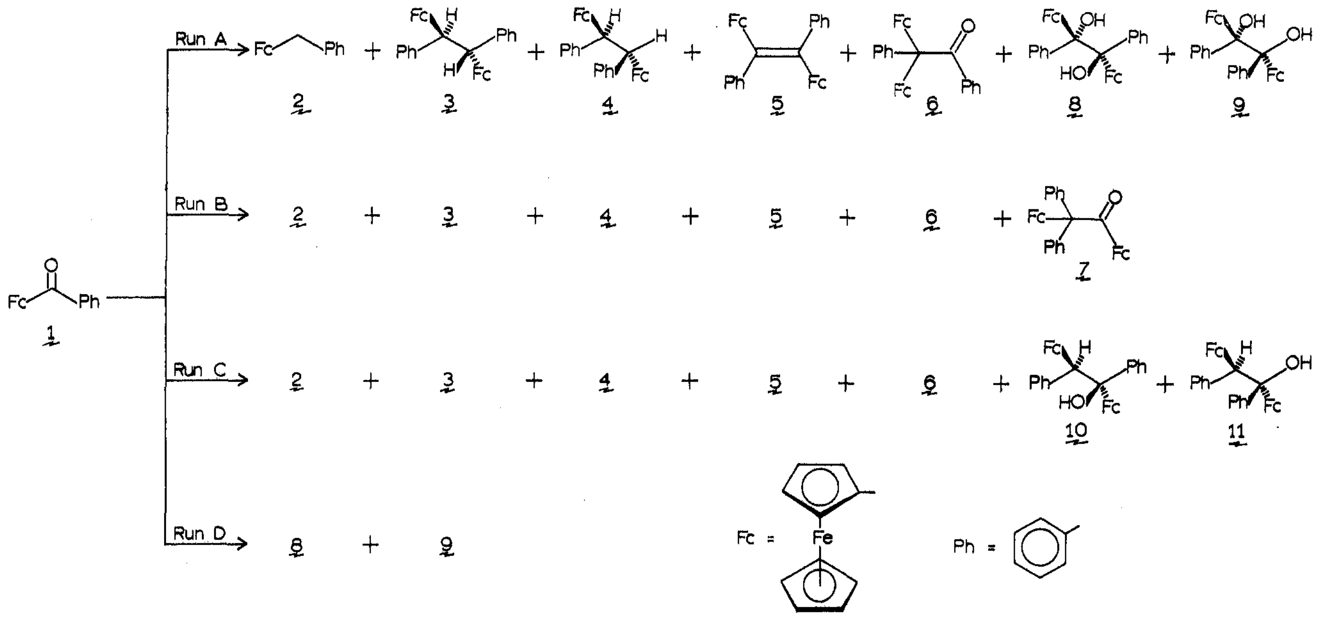

TABLE I

SUMMARY OF PRODUCTS

Run[a]	Products, % yield										Material balance, %[c]
	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**[b]	**11**[b]	
A	12.6	5.7	3.2	38.4	[d]	[e]	[d]	[d]	[e]	[e]	61.9
B	5.8	4.5	3.0	21.3	14.7	1.0	[e]	[e]	[e]	[e]	50.3
C	[d]	[d]	[d]	[d]	[d]	[e]	[e]	[e]	[f]	[d]	
D	[e]	[e]	[e]	[e]	[e]	[e]	40.1	23.1	[e]	[e]	80.4[g]

[a] See Experimental Section for reaction details. [b] Stereochemical assignments tentative; see Discussion. [c] Mole per cent of consumed benzoylferrocene as accounted for in terms of purified products. [d] Compound present, but amount not determined. [e] Presence not known. [f] Only a 10-mg purified sample of this difficult to handle compound was obtained. [g] Combined weight of chromatographically pure but unseparated pinacols.

number of reductions of this ketone under a variety of conditions and isolated nine bimolecular products, the majority of which are characterized for the first time.

Results

Four typical reactions are here considered; these (Scheme I and Table I) produced, in the aggregate, all nine of these products.

Run A (97°, 15 min) yielded pinacols **8** and **9**, showing that the stereomeric pinacols were formed rapidly and may thus be considered the principal source of the other bimolecular products. Run D (room temperature, 20 min) gave only pinacols **8** and **9**. These pinacols have been reported[8] to be unstable in solution, but solutions in oxygen-free benzene or carbon disulfide are reasonably stable. It was of interest to learn the relative stereochemistry of the two diastereomers which melted at 202–204 and 207–209°. The uncertainties surrounding choices of conformational preferences in the two isomers and the possibility of several different intramolecular hydrogen bonds (Scheme II) appeared to preclude use of the usual spectral methods for these assignments. In the meantime, relative configurations of the stereomeric ethanes **3** and **4** were established by the means discussed below, and suitable chemical connections were sought in order to correlate configurations of the pinacols with the ethanes.

Raney nickel catalyzed reduction[10] was tried, but each pinacol was cleaved to benzylferrocene (**2**). Each pinacol was also treated with lithium aluminum hydride in the presence of aluminum chloride,[11,12] but the chiral ethane **3** was found to be the major product in each case.

$$8 \xrightarrow[\text{AlCl}_3]{\text{LiAlH}_4} 3\ (55\%) + 2\ (19\%) + 6\ (8\%)$$

$$9 \xrightarrow[\text{AlCl}_3]{\text{LiAlH}_4} 3\ (51\%) + 2\ (17\%)$$

Relative configurational assignments of the pinacols were finally secured by carrying out their preparation from benzoylferrocene in the presence of the chiral solvent, (+)-(*S*)-1-methoxy-2-methylbutane (**12**).[13] The use of a chiral solvent or a chiral additive to effect asymmetric selection during a reaction has been carried out in a number of other cases.[1c] Its successful application in the present work provided unequivocal stereo-

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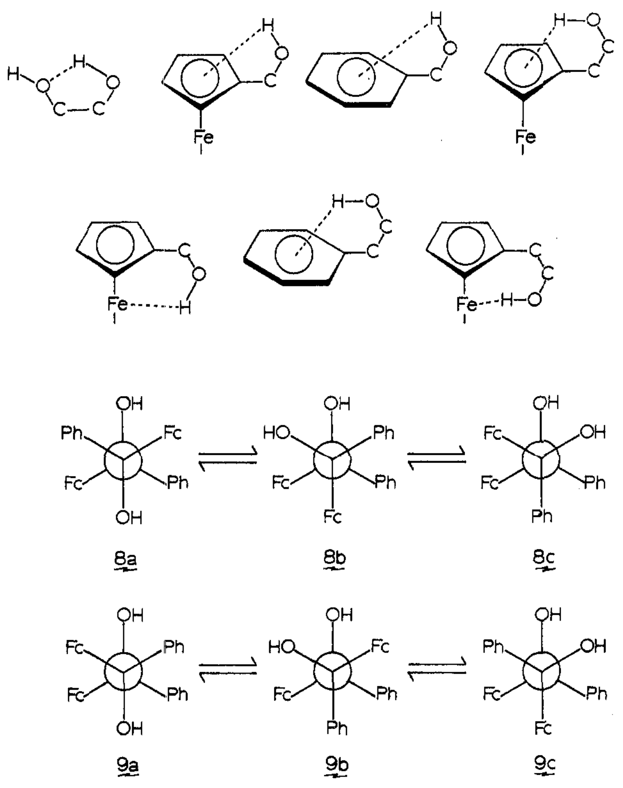
(10) D. J. Cram, *J. Amer. Chem. Soc.*, **76**, 4516 (1954); W. A. Bonner, *ibid.*, **81**, 3336 (1959); S. Mitsui, Y. Senda, and K. Donno, *Chem. Ind. (London)*, **32**, 1354 (1963); T. J. Leitereg and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 4011 (1968).

(11) This combination appears to be of general utility for effecting reduction of arylcarbinols; *cf* B. T. Brown and A. M. S. White, *J. Chem. Soc.*, 3755 (1957); R. F. Nystrom and R. A. Berger, *J. Amer. Chem. Soc.*, **80**, 2896 (1958); E. A. Hill and J. H. Richards, *ibid.*, **83**, 4216 (1961).

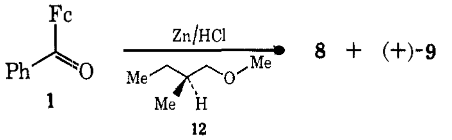
(12) Very recently M. J. A. Habib and W. E. Watts [*J. Chem. Soc. C*, 1469 (1969)] have provided examples in which the reduction occurs with retention of configuration.

(13) H. G. Rule, E. B. Smith, and J. Harrower, *J. Chem. Soc.*, 376 (1933).

SCHEME II

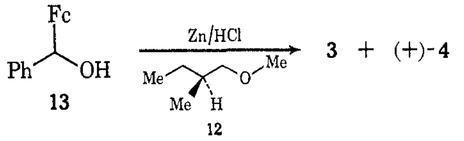


chemical designations for the isomeric pinacols as well as the isomeric ethanes. By taking advantage of the rapid formation of the pinacols, it was possible to avoid the complicating presence of other products by quenching a reaction mixture of benzoylferrocene, zinc dust, concentrated hydrochloric acid, and the chiral solvent **12** in aqueous base after 10 min to provide pure crystalline samples of each pinacol. Since the higher melting diastereomer (207–209°) was found to be optically active and the lower melting form (202–204°) was not, it followed that the former was the chiral isomer **9** or its mirror image, and that the latter was the achiral isomer **8**. In every case where the pinacols were found and separated, the amount of the achiral form always exceeded the chiral form.



The diastereomeric ethanes **3** and **4** were first isolated and characterized by Berger, McEwen, and Kleinberg in their work on the acid-catalyzed decomposition of ferrocenylphenylcarbinyl azide.[14] Both of these isomers were usually found in significant amounts in the Clemmensen reductions of benzoylferrocene. Here, as in the case of the pinacols, clear-cut assignments of relative stereochemistry followed directly from independent preparation of the isomeric ethanes under conditions that allowed for asymmetric selectivity. The successful procedure was modeled after the reductive coupling of ferrocenylphenylmethanol (**13**) carried out by Cais and Eisenstadt.[15] Treatment of (±)-ferrocenylphenylmethanol (**13**) in (+)-(*S*)-1-methoxy-2-methylbutane (**12**) with zinc dust and hydrochloric acid gave the lower melting diastereomeric ethane (mp 218–222°) in 45% yield and the higher melting isomer (mp 276–278°) in 31% yield. Of the two purified compounds, only the higher melting stereomer displayed optical activity, showing it to be the chiral configurational isomer **4** or its mirror image. Optical inactivity of the lower melting isomer corroborated its designation as the achiral form **3**. When this experiment was carried out using zinc amalgam instead of zinc dust, and using a higher proportion of the optically active solvent, the higher melting isomer was obtained in much lower material yield but with more than twice the dextrorotatory magnitude displayed by the chiral sample of the first experiment.[16]

As in the case of the diastereomeric pinacols, the amount of the achiral ethane **3** was found to exceed that of its diastereomer, not only in the reductive coupling reactions[18] but in the numerous Clemmensen reductions as well. It is also significant that in each of the various decompositions of ferrocenylphenylcarbinyl azide[14] amounts of what is now recognized as the achiral ethane **3** exceeded the amounts of chiral isomer **4**.[19]



1,2-Diferrocenyl-1,2-diphenylethene (**5**) was usually found to be the major bimolecular product of Clemmensen reduction of benzoylferrocene. It was previously prepared by Pauson and Watts[20] by treatment of benzoylferrocene with sodium diphenylphosphinite. Careful examination, in the present work, of a number of purified samples always revealed the olefin as chromatographically homogenous, strongly indicating the presence of only one of the two configurational possibilities. This conclusion was substantiated by conversion of the ethene to the corresponding ethane *via* hydroboration of the former, followed by treatment with propionic acid. This procedure did not give any detectable (tlc) achiral ethane **3** but produced only the chiral ethane **4** in good yield, accompanied by a small amount of benzylferrocene. Thus, not only did these results strongly suggest that only one configurational ethene was formed in Clemmensen reduction and in the method used by Pauson and Watts[20] but that the compound must be the *E*-[21] or *trans*-ethene **5**. The configurational assignment

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[14] A. Berger, W. E. McEwen, and J. Kleinberg, *J. Amer. Chem. Soc.*, **83**, 2274 (1961).

[15] M. Cais and A. Eisenstadt, *J. Org. Chem.*, **30**, 1148 (1965).

[16] In experiments where an optically active component is utilized and the results are interpreted on the basis of optical activity determined from a product, it is essential to assure that the latter is not contaminated with the former.[17] That the optical activity observed in the two substances of the present work was not due to contamination with the optically active solvent **12** is assured by the following facts: (a) careful purification before polarimeter measurements; (b) the diastereomeric partner, similarly purified in each case, was found to be optically inactive; and, although it happened to have the same rotatory direction, (c) the rotatory magnitude of each purified product significantly exceeded that of even the neat solvent.

[17] See J. E. Baldwin, R. E. Hackler, and R. M. Scott [*J. Chem. Soc. D*, 1415 (1969)] for additional comments on this point.

[18] This was also true in the orginal reductive coupling of **13**.[15]

[19] Isolation of the lower melting ethane (achiral), but failure to isolate the higher melting (chiral) isomer, by Rausch and Adams[9] may also be taken as part of this general pattern.

[20] P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 2990 (1963).

[21] Chemical Abstracts Staff, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

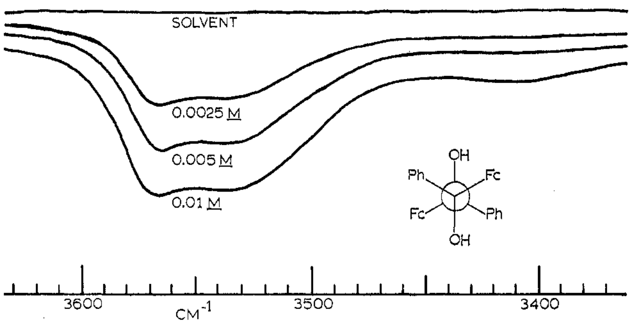


Figure 1.—Infrared spectra of the achiral pinacol **8**: Perkin-Elmer 621 grating spectrometer; 0.01, 0.005, and 0.0025 *M* in carbon disulfide; 1-cm cell.

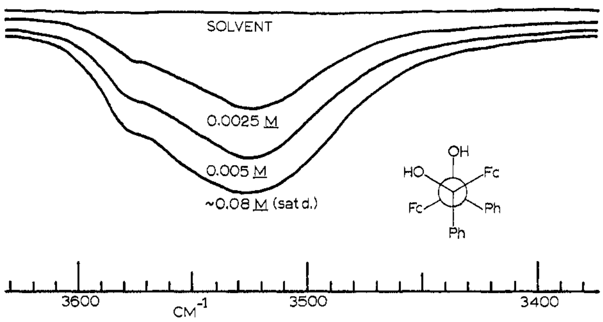
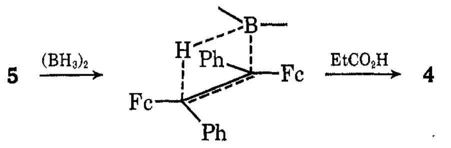


Figure 2.—Infrared spectra of the chiral pinacol **9**: 0.008, 0.005, and 0.0025 *M*.

follows from the well-documented[22] overall syn hydrogenation of the hydroboration–acid cleavage sequence.



The pinacolone, 2,2-diferrocenyl-1,2-diphenylethanone (**6**), was historically the first recognized bimolecular Clemmensen reduction product. Weliky and Gould[8] also showed that it was produced by acid-catalyzed rearrangement of the now recognized mixture of isomeric pinacols **8** and **9**. Despite the relative ease with which phenyl migrates in pinacol–pinacolone rearrangements, only the pinacolone **6** (ferrocenyl migration) has heretofore been reported.[5,6,8,9] In the present work (run B, 97°, 90 hr), the isomeric pinacolone **7** (phenyl migration) was isolated and characterized. The two ketones are readily distinguished by their melting points (**6**, 204–206°, and **7**, 245–250° dec) and their spectral properties; the important features of which are recorded in the Experimental Section. While additional aspects are to be treated in a subsequent paper, it should be noted here that **6**, the product of ferrocenyl migration, exceeded **7**, the product of phenyl migration, by a factor of about 15 in run B, although the ratio was lower when the individual pinacols **8** and **9** were allowed to undergo rearrangement.

Run C (room temperature, 5 hr) is notable because of the occurrence of the stereomeric alcohols, **10** and **11**. These previously undetected, extremely unstable alcohols supply an important link in the rationalization of bimolecular Clemmensen reduction of ferrocenyl ketones.

Discussion

It is of interest to appraise the relative degree of nonbonded interactions involving the phenyl and the ferrocenyl groups. The decision is not obvious from consideration of scale conformational models,[23] for along one of the dimensions phenyl is larger than ferrocenyl, while along another dimension the reverse is true. The results of the present study, however, may be consistently interpreted in terms of the ferrocenyl group possessing a significantly larger effective bulk than the phenyl group.

An interesting manifestation of this may be seen in the OH stretching regions of the infrared spectra determined from each of the stereoisomeric pinacols, **8** and **9**. In the reproduced spectra of Figures 1 and 2, neither the achiral pinacol **8** nor the chiral isomer **9** give any detectable amounts of free or nonbonded OH. In each case, however, complex absorptions, owing to concentration independent, intramolecular hydrogen bonds, between 3600 and 3500 cm^{-1}, predominate. These must be due to various combinations of the well-established types[24] illustrated in Scheme II and are consequently too complex to deal with.

The spectrum determined from the achiral pinacol (Figure 1), however, possesses a fairly broad, concentration dependent, band centered near 3420 cm^{-1} which must be due to intermolecular hydrogen bonding. Absorption of this type is absent in the spectra of the chiral isomer. Since **8a** (Scheme II) would be expected to be the most highly populated conformer of the achiral pinacol, it is reasonable to conclude that intermolecular hydrogen bonding appears to occur to a detectable extent only when the hydroxyl groups are in the anti relationship. Since absorption owing to intermolecular hydrogen bonding is absent in the chiral spectra, conformer **9a**, possessing a ferrocenyl–ferrocenyl gauche interaction, must not be significantly populated. Avoidance of the gauche ferrocenyl–ferrocenyl nonbonded interaction may also be seen in other results of the present study.

Reductive coupling of benzoylferrocene invariably gave the achiral pinacol **8** in greater amount than the chiral isomer **9**. This stereoselective manifestation may be accounted for in terms of a minimization of nonbonded interactions during coupling of the protonated benzoylferrocene species **14** or the radical **15** produced from it.[25] If in the two approaches, represented by **16** and **17** (Scheme III), the ferrocenyl groups are kept in a developing anti relationship, then, while each (**16** and **17**) possess two developing ferrocenyl–phenyl gauche interactions, **17** has in addition a phenyl–phenyl gauche interaction. The more favorable approach (**16**) leads to the more abundant stereomeric, achiral pinacol **8**.

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[22] H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, p 128 ff.

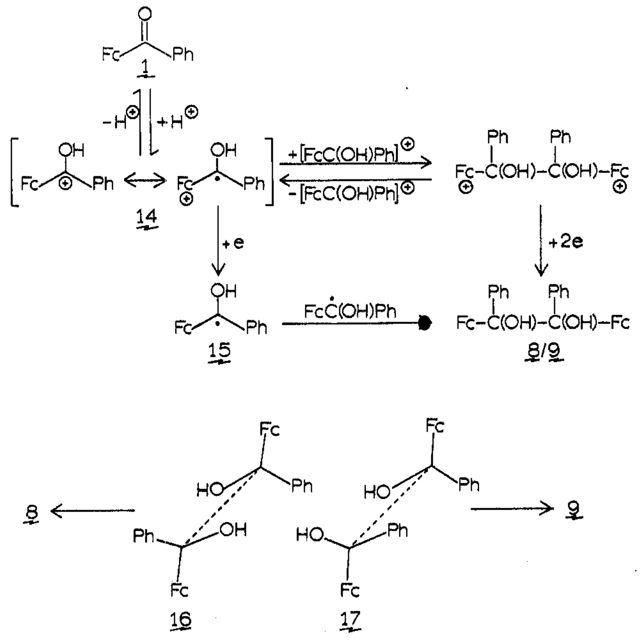
[23] S. I. Goldberg, *J. Chem. Educ.*, **43**, 554 (1966).

[24] D. S. Trifan and R. Bacskai, *J. Amer. Chem. Soc.*, **82**, 5010 (1960); E. A. Hill and J. H. Richards, *ibid.*, **83**, 4216 (1961); I. D. Campbell, G. Eglinton, and R. A. Raphael, *J. Chem. Soc. B*, 338 (1968); M. J. Nugent and J. H. Richards, *J. Amer. Chem. Soc.*, **91**, 6138 (1969).

[25] Cais and Eisenstadt[15] have argued that species like **14** and **18** contribute insignificantly to the formation of dimers. The evidence, however, does not appear to be a conclusive basis for rejection of the dimerization mechanism initially suggested by Rinehart and coworkers.[26]

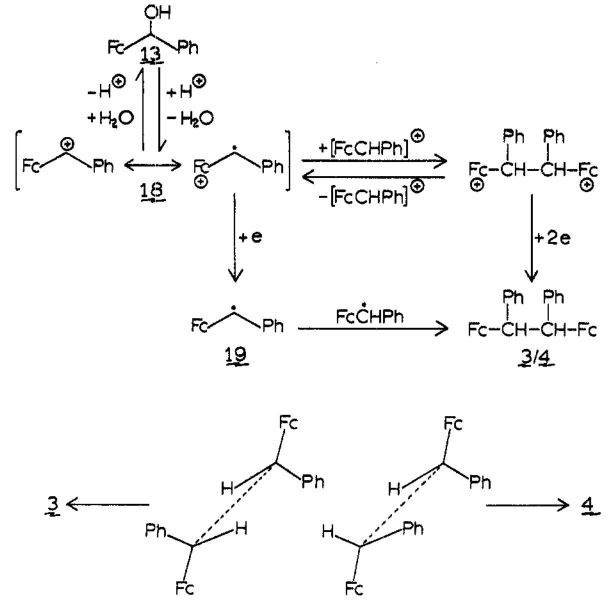
[26] K. L. Rinehart, Jr., C. J. Michejda, and P. A. Kittle, *J. Amer. Chem. Soc.*, **81**, 3162 (1959).

SCHEME III



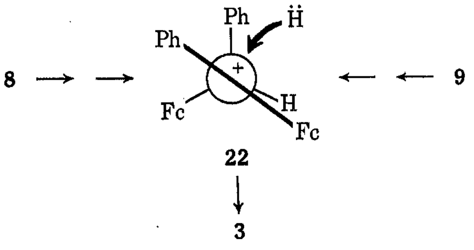
In a similar way the predominance of the achiral ethane **3** over the chiral form **4** in all of the examples of reductive coupling from ferrocenylphenylmethanol (**13**) may be accounted for (Scheme IV). Whether the species involved in the two idealized coupling approaches, **20** and **21**, are considered in terms of **18**, the cation radical,[25] or **19**, the radical, need not effect the argument. Minimization of nonbonded interactions favors **20**, which leads to the more abundant achiral ethane **3**.

SCHEME IV

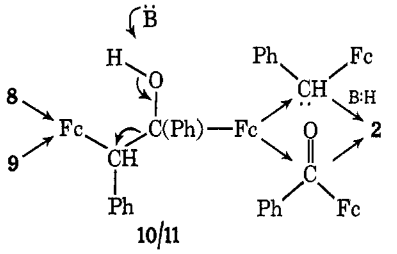


Avoidance of ferrocenyl–ferrocenyl nonbonded interaction during formation of 1,2-diferrocenyl-1,2-diphenylethene also appears to be the probable basis for production of only the trans isomer **5**.

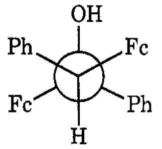
Both stereomeric pinacols, on treatment with lithium aluminum hydride and aluminum chloride, give the achiral ethane, suggesting that the steric outcome is independent of the first stage of reduction (which would give **10** or **11**) but is governed by conformational effects during the second stage. Both **10** and **11** would be expected to give cation **22** in which ferrocenyl is opposed to hydrogen, and hydride delivery to this ion should occur preferentially over phenyl, leading to the achiral ethane **3**.



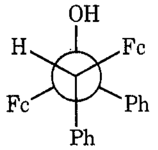
These reductions, however, were accompanied by a small amount of fragmentation and, to a lesser extent, rearrangement. If the alcohols (**10** and/or **11**) were indeed intermediates in the lithium aluminum hydride–aluminum chloride reduction of the pinacols, their tendency to fragment was not so great as it was found to be under basic or neutral conditions. For example, the only observable product when each pinacol was treated with freshly prepared Raney nickel was benzylferrocene. In light of the ease with which the alcohols, **10** and **11**, underwent fragmentation to benzylferrocene and benzoylferrocene, it is likely that the pinacols **8** and **9** were first reduced to the alcohols **10** and **11**, and these then fragmented[27] to benzylferrocene and benzoylferrocene followed by reduction of the latter to the former.



The great ease with which the alcohols **10** and **11** underwent fragmentation made them extremely difficult to handle and precluded rigorous assignments of stereochemistry. It was observed, however, that the alcohol with the lower R_f value (0.17 *vs.* 0.27) fragmented faster. Assuming that this difference is attributable to the difference in gauche interactions present in the most favorable conformation of the achiral and achiral alcohols (**10a** and **11a**, respectively), then **11a** with its additional phenyl–phenyl gauche interaction may be assigned to the less stable, lower R_f isomer.



10a



11a

While these assignments are considered to be tentative, they are strengthened slightly by the fact that the lower R_f alcohol, assigned as the chiral form **11a**, was

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(27) For similar examples of tertiary alcohol fragmentation, see D. J. Cram, W. D. Nielsen, B. Rickborn, L. K. Gaston, and H. Jäger, *J. Amer. Chem. Soc.*, **83**, 2174, 2178, 2183 (1961), and references cited therein.

also found to be the less soluble (hexane) partner, as was the case with the other chiral isomers **4** and **9**. In any case, the presence of **10** and **11** among the bimolecular reduction products provides an important contribution toward a reasonable explanation of the formation of the bimolecular reduction products.

Experimental Section

General.—Temperatures are uncorrected. Melting points were determined in open capillary tubes except where noted. Column (elution) chromatography was with Merck acid-washed alumina. Mixtures to be chromatographed were dissolved in the minimum volumes of benzene and added uniformly to the tops of the alumina columns which were previously prepared by the wet technique in hexane. Due to low solubilities of many of the compounds, it was necessary to use rather high weight ratios of alumina to mixture. These were usually of the order of 100:1. Thin layer chromatography (tlc) was a crucial analytical tool in this work. Glass plates, coated with silicic acid (Brinkmann Instruments Co., Cat. No. 7731), were used. Development solvents are cited along with the relevant R_f values. Visualization of spots on the developed plates required no additional treatment, since all of the ferrocene compounds are colored.

For the Clemmensen reductions, preparations of zinc amalgam (cited simply as amalgam) were carried out in the usual way[28] with the quantities of materials cited in parentheses: grams of zinc, grams of mercuric chloride, milliliters of water, and milliliters of concentrated hydrochloric acid, respectively. Two stirring assemblies, referred to as fast and slow, were used. The former signifies a four-bladed stirrer operated by a 2500-rpm motor, and the latter refers to a 250-rpm motor which operated a two-bladed stirrer.

Infrared (ir) spectra were determined with a Perkin-Elmer Model 337 spectrophotometer. In each case the sampling method is indicated along with the corresponding data. A Varian Model A-60 nuclear magnetic resonance (nmr) spectrometer was used to record ^{1}H nmr spectra at 60 Hz in solutions containing tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm under the δ convention relative to the TMS signal (0 ppm). For ultraviolet (uv) spectra, a Perkin-Elmer Model 202 spectrophotometer was used. Mass spectra were initially determined with an Associated Electrical Industries Model MS-9 instrument,[29] followed by use of a Hitachi Perkin-Elmer Model RMU-6 spectrometer.[30] Chiroptical (optical activity) measurements at 546 and 589 nm were carried out with Rudolph and Sons, Inc., polarimeters. Combustion analyses were made by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Clemmensen Reduction Products.—Given below are physical and spectral properties determined from each of the individual products isolated from the various Clemmensen reductions of benzoylferrocene (**1**) carried out in this study.

Benzylferrocene (**2**): mp 75–76° (lit.[5,6,8] mp 74.5–75.5°); mass spectrum *m/e* 276 (M$^+$); ir (CCl_4) 3080, 3060, 1097, 992 (ferrocenyl), 3030, 1602, 1498, 1063 (phenyl), 2920, 2848, and 1452 cm^{-1} (methylene); nmr ($CDCl_3$) δ 7.18 (5 H, s, protons of unsubstituted ferrocene ring), 4.06 (4 H, apparent s, protons of substituted ferrocene ring), and 3.68 (2 H, s, methylene protons).

Achiral 1,2-Diferrocenyl-1,2-diphenylethane (**3**):[31] mp 220–222° [lit.[15,32] mp 218–220° (α isomer) and 218°, respectively]; mass spectrum *m/e* 275 (highest observable ion[33]); ir (KBr) 3070, 3050, 1103, 998 (ferrocenyl), 3020, 1600, 1500, 1450 (phenyl), 2920 and 2890 cm^{-1} (methine); nmr ($CDCl_3$) δ 7.05 (10 H, apparent s, phenyl protons), 3.82 (4 H, m, α-ferrocene protons), 3.82 (4 H, m, β-ferrocene protons), 3.72 (2 H, apparent s, methine protons), and 3.68 (10 H, s, protons of unsubstituted ferrocene rings).

Chiral 1,2-Diferrocenyl-1,2-diphenylethane (**4**):[31] mp 276–280° [lit.[15] mp 276–280° (β isomer)]; mass spectrum *m/e* 275 (highest observable ion[33]); ir (KBr) 3070, 1103, 1000 (ferrocenyl), 3010, 1600, 1495, 1452 (phenyl), and 2900 cm^{-1} (methine); nmr ($CDCl_3$) δ 7.12 (10 H, apparent s, phenyl protons), 3.82 (4 H, m, α- and β-ferrocene protons), and 3.62 (12 H, apparent s, methine protons and protons of unsubstituted ferrocene rings).

(*E*)-1,2-Diferrocenyl-1,2-diphenylethene (**5**):[31] mp 278–280° (lit.[20] 278–280°); mass spectrum *m/e* 548 (M$^+$); ir (KBr) 3080, 3045, 1101, 1000 (ferrocenyl), 2020, 1600, 1497, 1450 (phenyl), and 1645 cm^{-1} (double bond?); nmr ($CDCl_3$) δ 4.02 (18 H, m, all ferrocene protons) and 7.43 (10 H, m, phenyl protons); uv max (95% C_2H_5OH) 218 (ϵ 39,000), 241 sh (11,000), 282 sh (4300), and 460 nm (350).

2,2-Diferrocenyl-1,2-diphenylethanone (**6**): mp 203–205° (lit.[5,8] 195–198° dec and 204–206°, respectively); mass spectrum *m/e* (rel intensity) 564 (15) (M$^+$) and 459 (20); ir (KBr) 3080, 1108 (ferrocenyl), 1600, 1490 (phenyl), and 1680 cm^{-1} (benzoyl carbonyl); nmr ($CDCl_3$) δ 7.45 (2 H, t, $J \sim 3$ Hz, *o*-benzoyl protons), 7.30 (8 H, m, remaining phenyl protons), 4.20 (4 H, t, $J \sim 2$ Hz, α-ferrocenyl protons), and 4.02 (14 H, apparent s, remaining ferrocenyl protons).

1,2-Diferrocenyl-2,2-diphenylethanone (**7**): mp 245–250° dec; mass spectrum *m/e* (rel intensity) 564 (20) (M$^+$) and 351 (100); ir ($CHCl_3$) 3090, 3060, 1110, 1003 (ferrocenyl), 3015, 3000, 1600, 1490, 1445 (phenyl), and 1670 cm^{-1} (ferrocenyl carbonyl); nmr ($CDCl_3$) δ 7.20 (10 H, m, phenyl protons), 4.25 (2 H, t, $J = 2$ Hz, α protons of ferrocenyl), 4.12 (2 H, t, $J \sim 2$ Hz, β protons of ferrocenoyl), 4.05 (12 H, apparent d, protons of unsubstituted rings of ferrocenoyl and ferrocenyl superimposed on α (?) protons of ferrocenyl), and 3.41 (2 H, t, $J \sim 2$ Hz, β (?) protons of ferrocenyl).

Anal. Calcd for $C_{34}H_{28}Fe_2O$: C, 72.37; H, 5.00. Found: C, 72.17; H, 5.19.

Chiral 1,2-Diferrocenyl-1,2-diphenyl-1,2-ethanediol (**9**):[31] mp 207–209° (oxygen-free, sealed capillary tube) [lit.[8] mp 125–140° (mixture of isomers)]; mass spectrum *m/e* 564;[34] ir (KBr) 3530 m, 3490 s, 3075 m, 3025 m, 3010 w, 1650 m, 1605 w, 1500 m, 1450 s, 1420 m, 1400 m, 1340 m, 1310 s, 1295 s, 1215 m, 1165 s, 1100 s, 1060 s, 1050 s, 1030 s, 1020 s, 995 s, 930 m, 915 w, 890 w, 865 w, 855 w, 845 m, 825 s, 815 s, 795 m, 780 w, 730 s, and 705 s cm^{-1}; nmr (CS_2) δ 7.07 (apparent d, $W = 3$ Hz, 10 H, phenyl protons), 4.03, 3.87, 3.78 (complex array, $W = 2$, 3 and 7 Hz, 8 H, α- and β-ferrocenyl protons), 3.62 (s, $W = 1$ Hz, 10 H, protons of unsubstituted ferocenyl rings), and 2.78 (s, $W = 1.5$ Hz, 2 H, hydroxyl protons).

Anal. Calcd for $C_{34}H_{30}Fe_2O_2$: C, 70.12; H, 5.19. Found: C, 69.50; H, 5.06.

Achiral 1,2-Diferrocenyl-1,2-diphenyl-1,2-ethanediol (**8**):[31] mp 202–204° (oxygen-free, sealed capillary tube) [lit.[8] mp 125–140° (mixture of isomers)]; mass spectrum *m/e* 564;[34] ir (KBr) 3540 s, 3500 m, 3380 w, 3075 s, 3040 m, 3010 w, 1630 m, 1600 w, 1500 m, 1450 s, 1410 m, 1390 m, 1340 m, 1285 m, 1200 m, 1170 m, 1155 m, 1105 s, 1060 s, 1025 s, 1000 s, 960 w, 910 w, 885 w, 820 s, 755 s, 725 s, and 700 s cm^{-1}; nmr (CS_2) δ 7.45, 7.00 (complex array, $W = 15$ and 25 Hz, 10 H, phenyl protons), 4.05 (m, $W = 8$ Hz, 4 H, α-ferrocenyl protons), 3.87 (m, $W = 7$ Hz, 4 H, β-ferrocenyl protons), 3.62 (s, $W = 1$ Hz, 10 H, protons of unsubstituted ferrocenyl rings), and 2.60 (s, $W = 1.5$ Hz, 2 H, hydroxyl protons).

Anal. Calcd for $C_{34}H_{30}Fe_2O_2$: C, 70.12; H, 5.19. Found: C, 69.88; H, 5.57.

1,2-Diferrocenyl-1,2-diphenylethanol (**10**):[35] mp 178–180°; mass spectrum *m/e* 566 (M$^+$); ir (benzene) 3100, 1105, 1000 (ferrocenyl), 1600, 1450 (phenyl), 2910 (methine), and 3520 cm^{-1} (hydroxyl); nmr ($CDCl_3$) δ 7.05 (10 H, m, phenyl protons), 3.95, 3.85 (8–9 H, both m, α- and β-ferrocenyl protons and methine proton), 3.75 (5 H, s, protons of unsubstituted rings of one ferrocenyl), 3.60 (5 H, s, protons of unsubstituted ring of a second ferrocenyl), and 2.68 (1 H, s, hydroxyl proton).

Anal. Calcd for $C_{34}H_{30}Fe_2O$: C, 72.12; H 5.34. Found: C, 71.50; H, 5.63.

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(28) E. L. Martin, *Org. React.*, **1**, 163 (1942).

(29) We are grateful to Dr. H. M. Fales, National Heart Institute, for these spectra.

(30) Acknowledgement of the grant awarded by National Science Foundation toward the purchase of this instrument is gratefully made.

(31) Experimental evidence upon which this stereochemical assignment rests is described under the appropriate heading of this section.

(32) A. N. Nesmeyanov, V. N. Drozd, and N. A. Rodionova, *Dokl. Akad. Nauk SSSR*, **160**, 355 (1965).

(33) This behavior of facile symmetric cleavage of the central carbon–carbon appears to be characteristic of tetraarylethanes, 1,1,2,2-tetraferrocenylethane (*m/e* 383) and 1,1,2,2-tetraphenylethane (*m/e* 167).

(34) Highest peak observed. It could not be determined whether this peak, which corresponds to M − 18, was due to thermal and/or mass spectral fragmentation.

(35) While good evidence was obtained for the presence of both diastereomeric forms (see experimental account and discussion), only this one (mp 178–180°), which appears to be the achiral isomer, was characterized.

Clemmensen Reductions of Benzoylferrocene.—Four typical Clemmensen reductions, leading together to the total array of compounds, are described. Spectra data and other criteria of identification, presented in the previous section, were applied in each instance. Assignments of the various tlc R_f values, established independently with authentic materials, are included.

A. Aqueous Toluene, Fast Stirrer, and Reflux Heating.—Benzoylferrocene (5.00 g, 17.1 mmol), dissolved in 35 ml of toluene, was added a mixture of amalgam (20 g, 2 g, 20 ml, 1 ml) and 10 ml of water, and the whole mixture agitated with the fast stirrer while concentrated hydrochloric acid (15 ml) was added (15 min) dropwise. Within 5 min after the addition was complete, the mixture had turned from red to yellow, signaling formation of the pinacols **8** and **9**. An aliquot (1 ml) was taken, and the yellow solid was collected on a filter and washed with ether. It had mp 125–140°, previously reported for what is now recognized (experiments described herein) as a mixture of the stereoisomeric pinacols. The sample spontaneously decomposed to benzoylferrocene when dissolved in benzene.

The reaction mixture was then heated under reflux (fast stirring maintained) and monitored by tlc [hexane–benzene, 3:2 (v/v)]. After 4 hr benzoylferrocene was absent, while the presence of each of the following substances was recognized: R_f 0.35 [2,2-diferrocenyl-1,2-diphenylethanone (**6**)], 0.60 [a mixture of achiral and chiral 1,2-diferrocenyl-1,2-diphenylethane (**3** and **4**, respectively)], 0.66 [*trans*-1,2-diferrocenyl-1,2-diphenylethene (**5**)], and 0.80 [benzylferrocene (**2**)].

The reaction mixture was allowed to cool to room temperature, poured into water, and extracted with benzene. The residue left after evaporation of the combined and dried ($MgSO_4$) benzene extracts was chromatographed on alumina. Elution with hexane–benzene [3:1 (v/v)] gave benzylferrocene (**2**), mp 74–76°, 595 mg (12.6% yield). Elution with hexane–benzene [1:1 (v/v)] gave an orange solid (2.31 g) which was shown to be a mixture of **3**, **4**, and **5**. The solid was washed with hexane to separate achiral 1,2-diferrocenyl-1,2-diphenylethane (**3**), mp 218–220°, 270 mg (5.7% yield). The residue left after removal of **3** was dissolved in hot benzene from which chiral 1,2-diferrocenyl-1,2-diphenylethane (**4**) crystallized, mp 278–280° dec, 150 mg (3.2% yield), and *trans*-1,2-diferrocenyl-1,2-diphenylethene (**5**), mp 278–280°, 1.80 g (38.4% yield), was obtained from the benzene supernatant.

B. Aqueous Toluene, Slow Stirrer, and Reflux Heating.—Benzoylferrocene (3.50 g, 12.1 mmol) was dissolved in toluene (12 ml) and added to a mixture of amalgam (12 g, 0.6 g, 12 ml, 0.6 ml) and water (6 ml). While the mixture was stirred (slow), concentrated hydrochloric acid (12 ml) was added dropwise (15 min) before the whole mixture was boiled under reflux for 90 hr. After the mixture was allowed to cool to room temperature, it was poured into water and extracted with benzene. As the combined and dried ($MgSO_4$) benzene extracts were being evaporated, a yellow solid formed. It was collected and shown to be chiral 1,2-diferrocenyl-1,2-diphenylethane (**4**), mp 278–280°, 100 mg (3.0% yield). The residue obtained from the benzene filtrate was chromatographed on alumina. A yellow fraction eluted with hexane–benzene [3:1 (v/v)] gave benzylferrocene (**2**), mp 73–75°, 213 mg (5.8% yield). Elution with hexane–benzene [1:1 (v/v)] led to a mixture (855 mg) of achiral 1,2-diferrocenyl-1,2-diphenylethane (**3**) and *trans*-1,2-diferrocenyl-1,2-diphenylethane (**5**), from which the former was separated by trituration with hexane, mp 200–220°, 147 mg (4.5% yield). The olefin **5** was obtained from the residue, mp 278–280°, 702 mg (21.3% yield). Elution of the column was continued with benzene. First a yellow band gave 2,2-diferrocenyl-1,2-diphenylethanone (**6**), mp 203–205°, 495 mg (14.7% yield). The second band was red, and it provided the isomeric pinacolone, 1,2-diferrocenyl-2,2-diphenylethanone (**7**), 245–250° dec, 37 mg (1.0% yield). Finally, ether eluted recovered benzoylferrocene, mp 106–108°, 32 mg (1% recovery).

C. Aqueous Toluene and Fast Stirrer at Room Temperature.—Benzoylferrocene (5.00 g, 17.1 mmol), dissolved in 35 ml of toluene, amalgam (20 g, 2.0 g, 20 ml, 1.0 ml), and 1 ml of water were stirred (fast) at room temperature while concentrated hydrochloric acid (20 ml) was added dropwise over a 15-min period. Almost immediately after the acid addition was complete, the reaction changed from red to yellow and remained yellow during the next 5 hr. A tlc monitor [hexane–benzene, 3:2 (v/v)] indicated the presence of eight components: R_f 0.06 [benzoylferrocene (**1**)], 0.17 [chiral (?) 1,2-diferrocenyl-1,2-diphenylethanol (**11**)], 0.27 [achiral (?) 1,2-diferrocenyl-1,2-diphenylethanol (**10**)], 0.35 [2,2-diferrocenyl-1,2-diphenylethanone (**6**)], 0.60 [achiral–chiral 1,2-diferrocenyl-1,2-diphenylethane (**3**) and (**4**)], 0.66 [*trans*-1,2-diferrocenyl-1,2-diphenylethene (**5**)], and 0.76 [benzylferrocene (**2**)].

The reaction mixture was decanted and passed through a filter on which was collected a yellow solid. This material was washed with water and with ether. It (1.81 g) was subsequently recrystallized from hexane (1.10 g, mp 125–150°). This material was unstable in solution. It was shown (tlc, color change to red) to transform to a mixture of benzoylferrocene, chiral (?) 1,2-diferrocenyl-1,2-diphenylethanol (**11**, R_f 0.17), and benzylferrocene (**2**). Concentration of the filtrate (reaction mixture) gave another sample of yellow solid: 150 mg; mp 125–140°; tlc [hexane–benzene, 3:2 (v/v)] R_f 0.06 [benzoylferrocene (**1**)], 0.27 [achiral (?) 1,2-diferrocenyl-1,2-diphenylethanol (**10**)], and 0.76 [benzylferrocene (**2**)]. Each cleanly resolved spot (R_f 0.17 and 0.27, separated plates) was transformed into a mixture of itself, benzoylferrocene, and benzylferrocene in the course of about 15 min on tlc plates. The slower moving (R_f 0.17) and less soluble isomer appeared to undergo this transformation more rapidly. Material (*ca.* 100 mg) from the second crystallization (R_f 0.27) was used in repeated preparative tlc.[36] The material obtained (18 mg) was carefully recrystallized from hexane to give achiral (?) 1,2-diferrocenyl-1,2-diphenylethanol (**10**), 10 mg, mp 178–180°.

D. Aqueous Ether and Fast Stirrer at Room Temperature.—A mixture of benzoylferrocene (500 mg, 1.71 mmol), dissolved in ether (5 ml), amalgam (2 g, 0.2 g, 4 ml, 0.2 ml), and water (0.5 ml) was stirred (fast) at room temperature while concentrated hydrochloric acid (2 ml) was added dropwise. Although a yellow precipitate formed in the reaction mixture within 5 min after the acid addition was complete, the stirring was continued for a total time of 15 min before the yellow material was collected in a filter. The solid, a mixture of the achiral and chiral pinacols **8** and **9**, was very sensitive to air. It was quickly washed with small portions of water and with small portions of ether before it was dried and stored in an evacuated desiccator, 400 mg, mp 125–140°.

Tlc analysis [hexane–ether, 3:2 (v/v)] showed the solid to consist only of two components, R_f 0.54 [chiral 1,2-diferrocenyl-1,2-diphenyl-1,2-ethanediol (**9**)] and 0.61 [achiral isomer **8**]. When the developed tlc plate was exposed to air, these yellow spots turned red quite rapidly. The red spots were separately scraped from the plate, and the material from each was washed from the silicic acid and re-spotted on a fresh tlc plate along with an authentic sample of benzoylferrocene. Development of the plate showed all three spots to be identical, and that benzoylferrocene was the only substance present in the two reclaimed samples.

It was found that the rates of fragmentation of the pinacols are relatively slow in a moderately basic medium. Accordingly, a major portion of the orginal mixture of isomeric pinacols was dissolved in a mixture of ether (200 ml), water (50 ml), and potassium hydroxide (2 g). After the solution was carefully concentrated to a volume of about 100 ml and kept near 0° for 1 hr, then the initial crop of well-formed yellow crystals was collected in a filter, washed with cold ether, and dried *in vacuo* to provide the chiral pinacol **9**: 115 mg; mp 207–209° (oxygen-free, sealed capillary); single tlc spot, R_f 0.54. Evaporation of the ethereal supernatant liquid to a volume of about 50 ml provided a second crop of equally well-formed yellow crystals which, after recrystallization, gave the achiral pinacol **8**: 200 mg; mp 202–204° (oxygen-free, sealed capillary); single tlc spot, R_f 0.61. Thus, the combined yield of the unseparated pinacols was near 80%. The crude chiral:achiral ratio was approximated as 1:3. See Figures 1 and 2 for details of the high-frequency ir regions.

Independent Preparation of 2,2-Diferrocenyl-1,2-diphenylethanone (6) and 1,2-Diferrocenyl-2,2-diphenylethanone (7).—A mixture of benzoylferrocene (500 mg, 1.71 mmol), dissolved in absolute ethanol (4 ml), and zinc dust (500 mg) was stirred (fast) at room temperature while absolute ethanol (4 ml), previously saturated with hydrogen chloride gas, was added dropwise over a 5-min period before the whole was boiled under reflux for 2 hr. When the reaction mixture had cooled to room temperature, it was poured into water and extracted with benzene. The com-

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[36] "Chrom-AR Sheet 500" (Mallinckrodt Chemical Works) was used. After each development the relevant band was cut out and eluted immediately so that the unstable alcohol, obtained by careful evaporation, could be stored and accumulated under inert conditions.

bined and dried ($MgSO_4$) extracts were evaporated to a residue which was chromatographed on alumina. Elution with hexane–benzene [3:1 (v/v)] gave benzylferrocene (**2**), 68 mg (14% yield), mp 73–75°. An orange solid (98 mg) was next eluted in hexane–benzene [1:1 (v/v)]. This material was shown by means of side-by-side tlc comparison with authentic compounds to be a mixture of *trans*-1,2-diferrocenyl-1,2-diphenylethene (**5**), achiral **3**, and chiral **4**. 2 2-Diferrocenyl-1,2-diphenylethanone (**6**), 242 mg (50.2% yield), mp 204–206°, was first eluted in benzene. It was followed by a red band from which was isolated the isomeric pinacolone, 1,2-diferrocenyl-2,2-diphenylethanone (**7**), 32 mg (6.6% yield), mp 245–250° dec.

Reductive Couplings of Ferrocenylphenylmethanol to Achiral and Chiral 1,2-Diferrocenyl-1,2-diphenylethanones (3 and 4). A. In Ether with Zinc Amalgam.—A mixture of ferrocenylphenylmethanol[37] (200 mg, 0.685 mmol), dissolved in ether (5 ml), amalgam (1 g, 0.2 g, 2 ml, 0.1 ml), and water (0.5 ml) was stirred (fast) at room temperature while concentrated hydrochloric acid (0.5 ml) was added dropwise (5 min). After 10 min, a tlc monitor [hexane–benzene, 3:1 (v/v)] showed the absence of starting material and indicated the presence of two components, R_f 0.35 (1,2-diferrocenyl-1,2-diphenylethane) and 0.58 (benzylferrocene). The ethereal phase was decanted, and the amalgam was washed with several portions of benzene which were combined with the original ether solution, and the whole mixture was washed with water and dried ($MgSO_4$). After the volume of the combined extracts was reduced to 5 ml, the concentrate deposited fluffy yellow crystals of chiral 1,2-diferrocenyl-1,2-diphenylethane (**4**), 51 mg (27% yield), mp 276–280°. The filtrate and ethereal washings were combined and evaporated to a solid which was carefully washed with several small portions of ether to dissolve the benzylferrocene. The residue gave achiral 1,2-diferrocenyl-1,2-diphenylethane (**3**), 92 mg (49% yield), mp 218–220°. The ether washings gave benzylferrocene (**2**), 27 mg (14% yield).

B. In (+)-(*S*)-1-Methoxy-2-methylbutane (12) with Zinc Dust.—Ferrocenylphenylmethanol[37] (200 mg, 0.685 mmol) was dissolved in (+)-(*S*)-1-methoxy-2-methylbutane[39] (2.5 ml) and added to a mixture of zinc dust (1 g) and water (0.5 ml). While this mixture was stirred (fast) at room temperature, concentrated hydrochloric acid (0.5 ml) was added dropwise. Within 5 min after the addition no starting material could be detected by tlc. The reaction mixture was worked up as described in the previous experiment (part A). The concentrated organic solution (10 ml) was kept at room temperature for 24 hr before collection of the initial yellow crystalline material which gave (+)-chiral-1,2-diferrocenyl-1,2-diphenylethane (**4** or mirror image), 58 mg (31% yield), mp 276–278°, $[\alpha]^{22}_{546}$ 26.1 ± 1.7° (*c* 0.176, C_6H_6). The supernatant liquid and washings were evaporated to a final volume of 5 ml, giving a crystalline precipitate which provided pure achiral 1,2-diferrocenyl-1,2-diphenylethane (**3**), 85 mg (45% yield), mp 218–220°, $[\alpha]^{22}_{546}$ 1.70 ± 1.70° (*c* 0.176, C_6H_6). Evaporation of the supernatant liquid gave a solid which was shown by tlc to be benzylferrocene (**2**), 18 mg (95% yield).

Another run was carried out. It differed in that amalgam (1 g, 0.2 g, 0.5 ml, 0.05 ml) was used with ferrocenylphenylmethanol (250 mg, 0.856 mmol) and 5 ml of the optically active ether (**12**). That procedure gave (+)-*chiral*-1,2-diferrocenyl-1,2-diphenylethane (**4**) in higher optical yield {$[\alpha]^{22}_{546}$ 57.3 ± 5.5° (*c* 0.183, C_6H_5)} but in lower material yield (20 mg, 8.5% yield).

Reductive Coupling of Benzoylferrocene in the Presence of (+)-(*S*)-1-Methoxy-2-methylbutane (12).—A mixture of benzoylferrocene 2(50 mg, 0.862 mmol), dissolved in (+)-(*S*)-1-methoxy-2-methylbutane[39] (5 ml), zinc dust (1 g), and water (0.5 ml) was stirred (fast) at room temperature while concentrated hydrochloric acid (1 ml) was added dropwise. After the addition was complete and the reaction mixture was stirred for an additional 10 min, it was poured into a mixture of ether (100 ml) and 1.8 *M* aqueous potassium hydroxide (50 ml) and boiled gently during 5 min. The liquid was then decanted from the zinc and evaporated until the ether volume was about 25 ml. The crystalline yellow precipitate that developed was collected and purified to give (+)-chiral-1,2-diferrocenyl-1,2-diphenyl-1,2-ethanediol (**9** or mirror image), 70 mg (28% yield), mp 207–209° (oxygen-free, sealed capillary), $[\alpha]^{21}_{546}$ 9.2 ± 1.0° (*c* 1.0, C_6H_6). The combined volumes of the supernatant liquid and washings were reduced to 10 ml, giving a yellow crystalline solid from which was obtained pure achiral 1,2-diferrocenyl-1,2-diphenyl-1,2-ethanediol (**8**), 80 mg (32% yield), mp 202–204° (oxygen-free, sealed capillary), $[\alpha]^{21}_{546}$ 0.80 ± 1.8° (*c* 0.50, C_6H_6).

Stereospecific Conversion of *trans*-1,2-Diferrocenyl-1,2-diphenylethene (5) to *threo*-1,2-Diferrocenyl-1,2-diphenylethane (4).—While a mixture of sodium borohydride (500 mg, 13.2 mmol) and *trans*-1,2-diferrocenyl-1,2-diphenylethene (50 mg, 0.091 mmol), dissolved in diglyme (50 ml), was stirred (magnetic) in a nitrogen atmosphere at room temperature, a solution of boron trifluoride etherate (2 ml) in diglyme (20 ml) was added dropwise during 30 min before the whole mixture was heated to, and maintained at, 100° for 2 hr. During this time the color of the reaction mixture changed from red to yellow. After the system was cooled to 30° and propionic acid (2.5 ml) was added dropwise over 15 min, the temperature was again raised to 100° and held there for 20 hr. The reaction mixture was then allowed to cool to room temperature when water (20 ml) was added slowly before the whole was poured into water (100 ml) and extracted with benzene. A tlc analysis [hexane–benzene, 3:2 (v/v)] of the combined, water-washed, and dried ($MgSO_4$) benzene extracts showed two components, R_f 0.60 (chiral **4**) and 0.75 (benzylferrocene **2**). Evaporation gave a yellow solid that was triturated with several small portions of methanol to remove the benzylferrocene. The residue gave chiral 1,2-diferrocenyl-1,2-diphenylethane (**4**), 29 mg (see below), mp 275–280°. The material obtained from evaporation of the combined methanol triturations was chromatographed carefully on alumina to give only benzylferrocene, 6.5 mg (26% yield), mp 74–76°, and an additional quantity of the chiral ethane **4**, 6.7 mg [35.7 mg total (71% yield)], mp 275–278°.

Treatment of the Chiral and Achiral Diols with Lithium Aluminum Hydride and Aluminum Chloride.—1,2-Diferrocenyl-1,2-diphenyl-1,2-ethanediol (**9**) (50 mg, 0.086 mmol) was added to a stirred (magnetic) mixture of lithium aluminum hydride (15 mg, 0.40 mmol) and anhydrous aluminum chloride (150 mg, 1.13 mmol), contained in dry ether (15 ml) in a nitrogen atmosphere. After 10 min, the mixture was boiled under gentle reflux for 50 min before tlc examination [hexane–benzene, 3:1 (v/v)]: R_f 0.05 [2,2-diferrocenyl-1,2-diphenylethanol (**10** and/or **11**)], 0.12 [2,2-diferrocenyl-1,2-diphenylethanone (**6**)], 0.33 [*erythro*-1,2-diferrocenyl-1,2-diphenylethane (**3**)], and 0.60 [benzylferrocene (**2**)]. After the mixture was hydrolyzed and the hydrolysate extracted with ether, the combined ether extracts were washed with water and dried ($MgSO_4$) before being evaporated to dryness. The residue was chromatographed on alumina. Initial elution was with hexane–benzene [3:2 (v/v)] which gave benzylferrocene (**2**), 8.0 mg (17% yield), mp 73–75°. The yellow band eluted in hexane–benzene [1:1 (v/v)] gave achiral 1,2-diferrocenyl-1,2-diphenylethane (**3**), 24 mg (51% yield), mp 218–220°. Development of the material remaining on the column with benzene produced two bands. The faster moving one (red) was eluted in benzene and gave 2,2-diferrocenyl-1,2-diphenylethanone (**6**), 4 mg (8% yield), mp 203–205°. The slower moving band (yellow) was eluted with ether to give diferrocenylphenylmethanol,[40] 3 mg (7% yield), mp 197–199° (lit.[8,20] 195–197°).

Corresponding treatment of the achiral diol **8** (100 mg, 0.172 mmol, in 25 ml of ether) was carried out by dropwise addition of the solution (10 min) to a stirred (magnetic) mixture of lithium aluminum hydride (15 mg, 0.40 mmol) and aluminum chloride (150 mg, 1.13 mmol) in 15 ml of ether at room temperature (nitrogen atmosphere). After addition the reaction mixture was heated under reflux for 30 min before it was examined by tlc: R_f 0.15 [pinacolone (**6**)], 0.36 (achiral ethane **3**), and 0.57 [benzylferrocene (**2**)]. Work-up and chromatography gave the three compounds: 8 mg (8% yield), 52 mg (55% yield), and 18 mg (19% yield), respectively.

Reductive Cleavage of Chiral and Achiral 1,2-Diferrocenyl-1,2-diphenyl-1,2-ethanediols with Raney Nickel.—A mixture of

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[37] Prepared by reduction of benzoylferrocene with lithium aluminum hydride in ether, mp 80–81° (lit.[6,8,38] mp 80.3–80.5°).

[38] W. Kuan-Li, E. B. Sokolova, L. A. Leites, and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 887 (1962).

[39] Prepared by treatment of a mixture of (−)-(*S*)-2-methyl-1-butanol and sodium hydroxide with methyl iodide at 100°. The optically active ether, **12**, was distilled from the reaction mixture. It was purified by an additional distillation, bp 90–92° (lit.[13] bp 91–94°), $\alpha^{21}{}_D$ 0.302° (lit.[13] $\alpha^{18}{}_D$ (0.29°).

[40] This material was shown to arise from cleavage of 2,2-diferrocenyl-1,2-diphenylethanol during alumina chromatography of the latter.

the chiral diol (50 mg, 0.086 mmol), dissolved in absolute ethanol (25 ml), and Raney nickel (freshly prepared[41] from 0.5 g of W-1 nickel-aluminum alloy) was stirred and boiled under reflux while contained under nitrogen. The reaction was periodically monitored by tlc [hexane-benzene, 3:2 (v/v)], which showed only a progressive increase in the formation of benzylferrocene (R_f 0.80). After 24 hr benzylferrocene was the only detectable compound present. Identical results were obtained when the experiment was repeated using the achiral diol.

Registry No.—**1,** 1272-44-2; **3,** 1278-05-3; **4,** 1278-04-2; **5,** 12284-11-6; **6,** 12258-13-8; **7,** 12504-69-7; **8,** 12504-73-3; **9,** 12504-72-2; **10,** 12504-70-0; **11,** 12504-71-1.

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The Photochemistry of Aryl Alkyl Carbonates. I. The Chlorophenyl Ethyl Carbonates

EDWARD A. CARESS* AND IRA E. ROSENBERG[1]

Department of Chemistry, The George Washington University, Washington D. C. 20006

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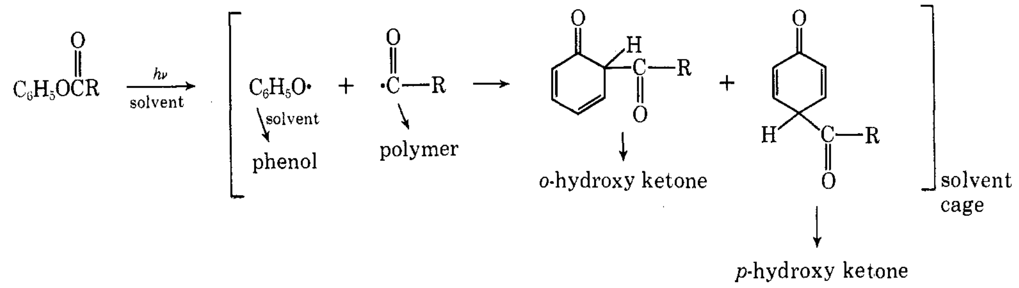
The photochemistry of the three chlorophenyl ethyl carbonates has been examined. The major process occurring is photodechlorination to give phenyl ethyl carbonate which subsequently undergoes a photo-Fries type of rearrangement. A minor process observed is the photosolvolysis of the chloride. The mechanisms of the reactions are discussed and the quantum yields are reported.

The Fries reaction is a well-known method for preparing aryl ketones from phenolic esters. The photo-Fries reaction is a less well-known but well-established method for effecting the same conversion.[2-7] The mechanism most often suggested for the reaction was proposed by Kobsa[4] and involves a homolytic cleavage of the carbonyl carbon-oxygen bond after the excitation of the ether molecule.



Pac and Tsutsumi[8] have reported that phenyl ethyl carbonate undergoes a photo-Fries type of reaction to give products analogous to those obtained in the photolysis of phenolic esters. Products that they identified were ethyl salicylate, ethyl *p*-hydroxybenzoate, and phenol. We have been investigating the photochemical reactions of a variety of aryl alkyl carbonates and can confirm Pac and Tsutsumi's results.

One way of investigating the mechanism of the photolysis of aryl alkyl carbonates is to examine the effect of placing various substituents on the aromatic ring. The type of substituent (electron attracting or electron repelling) and the position of the substituent relative to the reactive site have been shown to influence greatly the mode of photochemical reaction in aryl compounds.[9] Among the substituents chosen for this investigation was chlorine. In this paper we will discuss the observations that we made on the photochemical reaction of the chlorophenyl ethyl carbonates.

Results

The photolyses were performed by irradiating a solution of the chlorophenyl ethyl carbonate in isopropyl alcohol with a high-pressure mercury lamp using a Corex filter. The photolysis of the chlorophenyl ethyl carbonates (**1a–c**) gave phenyl ethyl carbonate (**2**) as the major product in each case. [The phenyl ethyl carbonate, as it was formed, was photolyzed to give phenol (**3**), ethyl salicylate (**4**), and ethyl *p*-hydroxybenzoate (**5**).] Two other products (**6** and **7**) were found; they appear to result from the interaction of the solvent with the chlorophenyl ethyl carbonate.

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