reaction of *tert*-butylmagnesium chloride (0.35 mol) with *p-tert*-butylbenzoyl chloride (0.40 mol) in refluxing ether. After hydrolysis and recovery of considerable acid the product was distilled to give a center cut of **1b** (6.86 g, 0.0314 mol, 9%): bp 84–87° (0.4 Torr) [lit.[15] mp 103–106° (1 Torr)]; nmr (CCl_4) δ 1.32 (s, sharp, 18, both *tert*-Bu), 7.1–7.8 (m, 4, aromatic); nmr (benzene) δ 1.21 and 1.30 (each s, 9, *tert*-Bu), aromatic obscured. The higher boiling distillation fractions included a solid which could not be identified.

***p-tert*-Butylphenyl-*tert*-butylcarbinol (7)** was obtained from the lithium aluminum hydride reduction of **1b**. After recrystallization from pentane at −25°, **7** was obtained as white prisms, mp 90–90.5°.

Preparation of Aryl-*tert*-butylneopentyl- and -dineopentylcarbinols.—*tert*-Butylneopentyl[16] and dineopentyl[17] ketones were prepared by the methods of Whitmore. Phenyllithium was made from lithium metal and bromobenzene in ether and *p*-anisyllithium, *p*-chlorophenyllithium, and *p*-trifluoromethylphenyllithium from *n*-butyllithium and the corresponding bromide. To a solution of the ketone in ether was added a solution of the aryllithium at about −20° under nitrogen atmosphere with vigorous stirring. After standing for 3 hr, the mixture was poured into an ice-cold aqueous ammonium chloride solution and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and evaporated to give an α-arylcarbinol. Yields were satisfactory in the case of phenyl derivatives, those for the anisyl-, chlorophenyl-, and trifluoromethylphenyl compounds were not, and the carbinols were isolated from the reaction mixture by thin layer chromatography. All the carbinols thus obtained gave satisfactory analyses and ir and nmr spectra consistent with the structures: **8**, bp 85° (2 mm), 89% yield; **9**, bp 94° (2 mm), 83%; **10**, mp 77–78°, 31%; **11**, mp 63–64°, 44%; **12**, mp 77–78.5°, 40%; **13**, mp 103–104°, 31%; for **14**, mp 53–54°, 43%.

Registry No.—**1a**, 938-16-9; **1b**, 22583-66-0; **2**, 3835-64-1; **3**, 21811-48-3; **4**, 34235-13-7; **5**, 34235-14-8; **6**, 15656-90-3; **7**, 34235-16-0; **8**, 34235-17-1; **9**, 34235-18-2; **10**, 34235-19-3; **11**, 34235-20-6; **12**, 34235-21-7; **13**, 34235-22-8; **14**, 34235-23-9; **15**, 1989-25-9; DMSO, 67-68-5; Eu(DPM)$_3$, 15522-71-1.

Acknowledgments.—Acknowledgments are made to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to Dr. K. Tori, Mr. M. Takasuga, and Miss Y. Yoshimura, who have carried out spectral determinations at Shionogi and given some helpful comments. Initial experiments on this topic were reported in the Ph.D. Thesis of T. T. T., Harvard University, 1964, for which Professor P. D. Bartlett provided thoughtful guidance.

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[16] F. C. Whitmore, J. S. Whitaker, W. A. Mosher, O. N. Breivik, W. R. Wheeler, C. S. Miner, Jr., L. H. Sutherland, R. B. Wagner, T. W. Clapper, C. E. Lewis, A. R. Lux, and A. H. Popkin, *ibid.*, **63**, 643 (1941).

[17] F. C. Whitmore, C. D. Wilson, J. V. Capinjola, C. O. Tongberg, G. H. Fleming, R. V. McGrew, and J. N. Cosby, *ibid.*, **63**, 2035 (1941).

Steric Crowding in Organic Chemistry. III. Spectral Properties, Conformations, and Reactivities of Highly Substituted Ferrocenylcarbinols[1]

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The preparation of a series of highly substituted ferrocenylcarbinols FcCRR'OH (**2–8**) has been accomplished. The hydroxyl stretching frequencies of the alcohols in CCl_4 solution showed bands in the region 3560–3583 cm^{-1} which were interpreted in terms of iron-bonded conformations, whereas bands at 3632 cm^{-1} were assigned to nonbonded conformations. Derivatives of the tertiary ferrocenyl carbinols could not be prepared, but the reactivity of the carbinols with acid to form cations was determined. *tert*-Butylferrocenylcarbinyl acetate (**10**) was prepared and found to undergo hydrolysis at a rate 4900 times as slow as methylferrocenylcarbinyl acetate. The depressed reactivity of **10** was attributed to steric hindrance of resonance stabilization.

The reactivity of α-arylcarbinols and their derivatives to form carbonium ions has been a topic of intensive investigation, particularly the electronic effect of substituents on the stability of the positive charge.[3,4] The stabilization by the ferrocenyl substituent is quite large,[4] but there has been considerable controversy as to whether the mode of stabilization by this group involves only hyperconjugative participation of bonding electrons[4h,i] or whether the nonbonding orbitals on iron are also significantly involved.[4a–d] The role of bulky substituents which prevent efficient overlap between the developing p orbital of the carbonium ion and the π system of the aromatic ring has also been examined in phenyl-substituted compounds.[5]

The spectroscopic properties of α-ferrocenylcarbinols have also been instructive regarding configurations and conformations of these compounds, as investigated by infrared[6a,b] and nmr[6c] measurements.

The present investigation was designed to elucidate the effect of very bulky substituents on the spectral properties and reactivity of α-ferrocenylcarbinols, and complements the investigation of the spectral proper-

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[1] Part II: F. H. Hon, H. Matsumura, H. Tanida, and T. T. Tidwell' *J. Org. Chem.*, **37**, 1778 (1972).

[2] (a) National Science Foundation Summer Undergraduate Research Participant, 1971. (b) University of South Carolina.

[3] (a) E. A. Hill, M. L. Gross, M. Stasiewicz, and M. Manion, *J. Amer. Chem. Soc.*, **91**, 7381 (1969); (b) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958); (c) W. S. Trahanovsky and D. K. Wells, *ibid.*, **91**, 5870, 5871 (1969).

[4] (a) E. A. Hill and J. H. Richards, *ibid.*, **83**, 3840, 4216 (1961); (b) D. W. Hall, E. A. Hill, and J. H. Richards, *ibid.*, **90**, 4972 (1968); (c) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Lett.*, 1695 (1966); (d) D. S. Trifan and R. S. Bacskai, *ibid.*, No. 13, 1 (1960); (e) G. Gokel, P. Hoffmann, H. Klusacek, D. Marquarding, E. Ruch, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **9**, 64 (1970); (f) M. J. A. Habib and W. E. Watts, *J. Chem. Soc. C*, 2552 (1970); (g) E. A. Hill, *J. Organometal. Chem.*, **24**, 457 (1970); (h) T. T. Tidwell and T. G. Traylor, *J. Amer. Chem. Soc.*, **88**, 3442 (1966); (i) T. G. Traylor and J. G. Ware, *ibid.*, **89**, 2304 (1967); (j) E. A. Hill and R. Wiesner, *ibid.*, **91**, 509 (1969); (k) J. Feinberg and M. Rosenblum, *ibid.*, **91**, 4324 (1969); (l) R. E. Davis, H. D. Simpson, N. Grice, and R. Petit, *ibid.*, **93**, 6688 (1971); (m) R. Gleiter and R. Seeger, *Helv. Chim. Acta*, **54**, 1217 (1971).

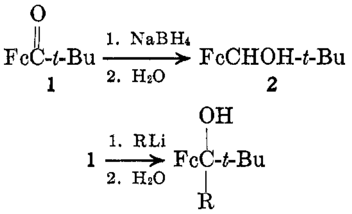
[5] (a) S. Winstein and B. K. Morse, *J. Amer. Chem. Soc.*, **74**, 1133 (1952); (b) G. Baddeley, J. Chadwick, and H. T. Taylor, *J. Chem. Soc.*, 2405 (1954); (c) J. Grimaud and A. Laurent, *Bull. Soc. Chim. Fr.*, 787 (1969).

[6] (a) D. S. Trifan and R. Bacskai, *J. Amer. Chem. Soc.*, **82**, 5010 (1960); (b) A. W. Baker and D. E. Bublitz, *Spectrochim. Acta*, **22**, 1787 (1966); (c) P. Reich-Rohrwig and K. Schlögl, *Monatsh. Chem.*, **99**, 2175 (1968).

ties[1] and reactivities[7] of α-phenylcarbinols with bulky substituents.

Results

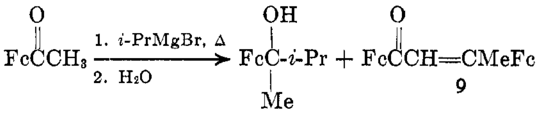
The *tert*-butylferrocenylcarbinols **2**–**7** were prepared either by reduction of *tert*-butyl ferrocenyl ketone (**1**) to give *tert*-butylferrocenylcarbinol (**2**) or by reaction of the appropriate alkyllithium with **1** (the ferrocenyl substituent is abbreviated Fc in this paper). Methylisopropylferrocenylcarbinol (**8**) was prepared by addition of isopropylmagnesium bromide to acetylferrocene; the aldol product **9** was also obtained in this reaction.



$$\underset{\mathbf{1}}{\mathrm{Fc\overset{\overset{O}{\|}}{C}\text{-}\mathit{t}\text{-}Bu}} \xrightarrow[\text{2. } H_2O]{\text{1. NaBH}_4} \underset{\mathbf{2}}{\mathrm{FcCHOH\text{-}\mathit{t}\text{-}Bu}}$$

$$\mathbf{1} \xrightarrow[\text{2. } H_2O]{\text{1. RLi}} \mathrm{Fc\overset{\overset{OH}{|}}{\underset{\underset{R}{|}}{C}}\text{-}\mathit{t}\text{-}Bu}$$

3, R = Me
4, R = Et
5, R = *i*-Pr
6, R = *t*-Bu
7, R = neoPn



$$\mathrm{Fc\overset{\overset{O}{\|}}{C}CH_3} \xrightarrow[\text{2. } H_2O]{\text{1. } i\text{-PrMgBr, } \Delta} \underset{\mathbf{8}}{\mathrm{Fc\overset{\overset{OH}{|}}{\underset{\underset{Me}{|}}{C}}\text{-}\mathit{i}\text{-}Pr}} + \underset{\mathbf{9}}{\mathrm{Fc\overset{\overset{O}{\|}}{C}CH{=}CMeFc}}$$

8

The hydroxyl stretching frequencies of all the alcohols were measured in dilute solutions in carbon tetrachloride and are summarized in Table I. In selected cases these were examined over a tenfold concentration range and shown to be independent of concentration, although at higher concentrations intermolecular hydrogen bonds could be observed. The chemical shifts of the hydroxyl protons for the ferrocenylcarbinols were not determined in dimethyl sulfoxide solutions as was done for the corresponding phenyl compounds, because they were insufficiently soluble in DMSO for strong signals to be observed, and also because the signals were anticipated to fall in the region of the spectrum where the ferrocenyl hydrogens absorb.

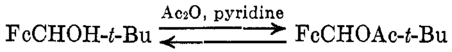
Table I

Hydroxyl Stretching Frequencies of Ferrocenylcarbinols (FcCRR′OH)[a,b]

Compd	R	R′	$\nu_{\max}$,[a] cm^{-1}
2	*t*-Bu	H	3632 (sh)[c] 3583
3	*t*-Bu	Me	3581
4	*t*-Bu	Et	3573
5	*t*-Bu	*i*-Pr	3573
6	*t*-Bu	*t*-Bu	3632 (4) 3579 (1)
7	*t*-Bu	neoPn	3574
8	*i*-Pr	Me	3560

[a] CCl_4 solutions, 0.2 *M*, relative intensities in parenthesis. Unchanged on dilution. [b] For comparison, ferrocenylcarbinol, methylferrocenylcarbinol, and dimethylferrocenylcarbinol display hydrogen bonds to the upper π face of ferrocene at 3620, 3613, and 3608 cm^{-1}, respectively, and iron-bonded hydroxyls at 3576, 3575, and 3571 cm^{-1}, respectively. None of these compounds show clearly resolved free hydroxyls, but β-ferrocenylethanol displays a free band at 3632 cm^{-1}, and ferrocenylmethanol has a shoulder at 3635 cm^{-1} (ref 6a and D. S. Trifan, private communication). [c] Shoulder on 3583 cm^{-1} band.

The ferrocenyl compounds were examined for their reactivity in carbonium ion forming reactions. The conversion of **2** to the acetate **10** for solvolysis studies required refluxing with acetic anhydride–pyridine, in contrast to ferrocenylmethylcarbinol, which reacts at low temperature.[8] The rates of hydrolysis of **10** to reform **2** were measured in aqueous acetone and are summarized in Table II. Attempts to prepare acetates or methyl ethers of the tertiary alcohols **3** and **6** were uniformly unsuccessful, yielding the parent alcohols or olefins instead. The high stability of the tertiary ferrocenyl carbonium ions apparently renders these derivatives quite unstable.



$$\underset{\mathbf{2}}{\mathrm{FcCHOH\text{-}\mathit{t}\text{-}Bu}} \underset{H_2O,\ \Delta}{\overset{Ac_2O,\ \text{pyridine}}{\rightleftarrows}} \underset{\mathbf{10}}{\mathrm{FcCHOAc\text{-}\mathit{t}\text{-}Bu}}$$

2 **10**

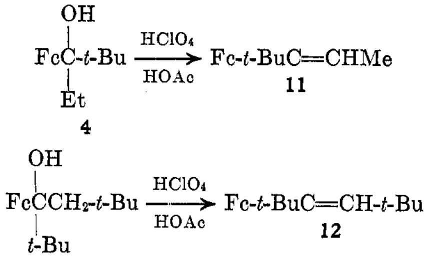
Table II

First-Order Rate Constants for Hydrolysis of α-Alkylferrocenylcarbinyl Acetates (FcCHROAc) in 60:40 Acetone–Water

R	Temp, °C	k_1, sec^{-1}	k_{rel}	Δ*H**, kcal/mol	Δ*S**, eu
t-Bu	84.8	2.16×10^{-4}		20.9	−17
(**10**)	69.9	4.97×10^{-5}			
	54.5	1.29×10^{-5}			
	0[a]	1.69×10^{-8}	1.0		
Me[b]	0	8.35×10^{-5}	4.9×10^{3}	19.0[c]	−13[c]

[a] Extrapolated. [b] Reference 4a. [c] In 80% acetone.

Since derivatives suitable for solvolysis studies could not be prepared, the reactivities of the alcohols **4**–**7** were examined by reaction with 0.07 *M* perchloric acid in acetic acid. The corresponding olefins resulting from dehydration were formed from **4** and **7**; these olefins appeared to be single isomers by nmr but the stereochemistry around the double bond was not established.



$$\mathrm{Fc\overset{\overset{OH}{|}}{\underset{\underset{Et}{|}}{C}}\text{-}\mathit{t}\text{-}Bu} \xrightarrow[\text{HOAc}]{HClO_4} \underset{\mathbf{11}}{\mathrm{Fc\text{-}\mathit{t}\text{-}BuC{=}CHMe}}$$

4

$$\mathrm{Fc\overset{\overset{OH}{|}}{\underset{\underset{\mathit{t}\text{-}Bu}{|}}{C}}CH_2\text{-}\mathit{t}\text{-}Bu} \xrightarrow[\text{HOAc}]{HClO_4} \underset{\mathbf{12}}{\mathrm{Fc\text{-}\mathit{t}\text{-}BuC{=}CH\text{-}\mathit{t}\text{-}Bu}}$$

7

After about 30 min reaction time, **4** and **7** gave 20 and 51% recovered starting material, respectively, whereas the isopropyl compound **5** disappeared with a half-life of about 3 min under the same conditions. The product from **5** was an apparent mixture that could not be separated by column chromatography nor identified by spectral examination. Di-*tert*-butylferrocenylcarbinol (**6**) reacted completely within 1 min and gave a mixture which was separated by preparative thin layer chromatography and shown to consist of 2-ferrocenyl-3,3,4,4-tetramethyl-1-pentene (**13**), methylisopropylferrocenylcarbinol (**8**), and dimethylferrocenylcarbinol (**14**)

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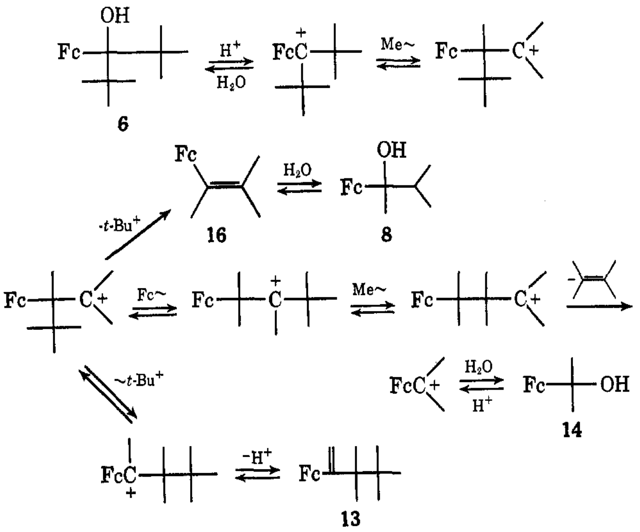
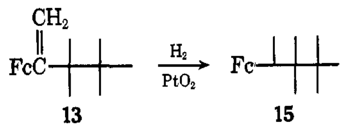
(7) H. Tanida, *et al.*, unpublished work.

(8) F. S. Arimoto and A. C. Haven, Jr., *J. Amer. Chem. Soc.*, **77**, 6295 (1955).

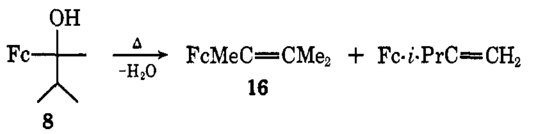
CHART I
ACID-CATALYZED REARRANGEMENT OF
DI-*tert*-BUTYLFERROCENYLCARBINOL (6)



(Chart I). The structure of **13** was established by spectral means and by hydrogenation to **15**, which also



displayed the expected spectral properties. Carbinol **8** from the reaction above was an oil identical with that prepared from acetylferrocene and isopropylmagnesium bromide. The compound could not be induced to crystallize, but on attempted distillation was dehydrated to the solid olefin **16** which was fully characterized.

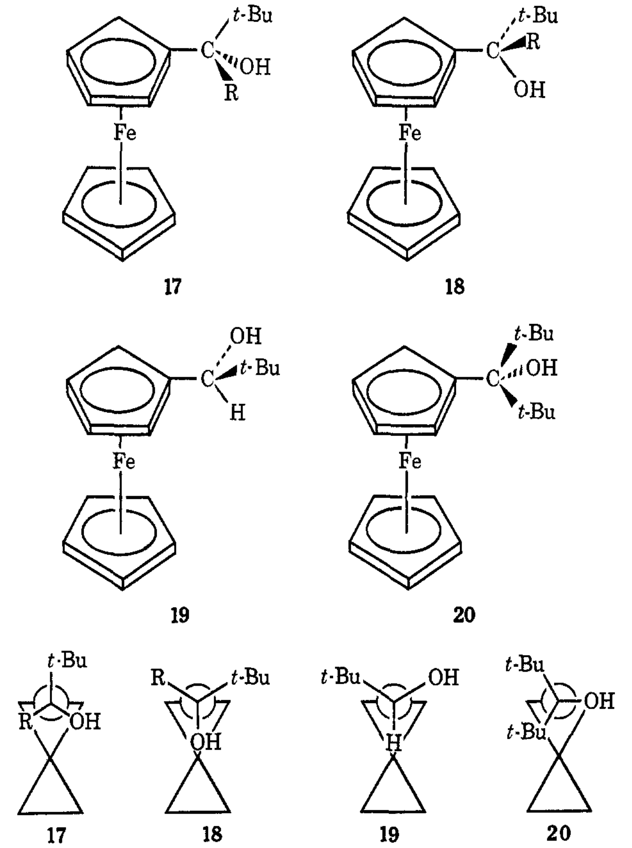


Weak signals in the nmr of **16** showed that a trace of the isomeric 2-ferrocenyl-3-methyl-1-butene was probably also present.

Discussion

The infrared spectra of the ferrocenylcarbinols all show a band at low frequency (3560–3583 cm^{-1}) in the region assigned to hydrogen bonding between the hydroxyl and nonbonding[6a,b] or bonding[9] orbitals of the iron. In the case of α-phenylcarbinols there is some question as to whether the infrared band which often appears in the region 3600–3625 cm^{-1} is due to an intramolecularly hydrogen bonded species or whether it arises from an unbonded rotamer.[1] The much larger shifts in the ferrocenyl derivatives leave little doubt that in these compounds such bonding does occur, probably in conformations such as **17** or **18** (Chart II). When R = H or *t*-Bu the nonbonded conformations **19** or **20**, respectively, are also significant. For compound **8** the isopropyl group is the largest substituent and occupies the position of the *tert*-butyl in **17** or **18**.

CHART II
CONFORMATIONS OF FERROCENYLCARBINOLS



The solvolytic properties of *tert*-butylferrocenylcarbinyl acetate (**10**) (Table II) show a drastic decrease in first-order solvolysis rate relative to the methyl-substituted compound. The release of strain in an S_N1 transition state for such a highly substituted derivative would have been expected to give a significantly accelerated rate; for example, di-*tert*-butylcarbinyl tosylate solvolyses 320 times faster than isopropyl tosylate in formic acid.[10] This steric acceleration decreases in more nucleophilic solvents, which give fast k_s reactions on isopropyl derivatives, but even in the highly nucleophilic aqueous solvents used for the ferrocene solvolyses the reactions consistently proceed with retention of configuration[4a,d,e] and surely involve a k_Δ process. Therefore, there is a rate-retarding effect for **10** of much more than the observed factor of 4900. This rate deceleration can be attributed to the steric repulsion of the *tert*-butyl by the ring in the transition state for exo departure of the acetate. This transition state suffers from the same unfavorable interactions which force the conformations **17** (or **18**) and **19** for the corresponding alcohol. Alternatively, the reaction might occur with endo departure of the leaving group, which is known to be less favorable in constrained systems by a factor of 2500.[4a,d] In the comparable phenyl compounds *tert*-butylphenylcarbinyl chloride is less reactive than methylphenylcarbinyl chloride in 80% ethanol at 50° by a factor of 490,[5a] which was attributed to steric interference of resonance by repulsion between the ortho hydrogens and the *tert*-butyl group.

The noticeable increase in reactivity of the ferro-

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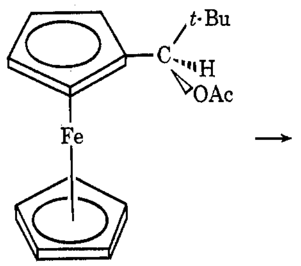
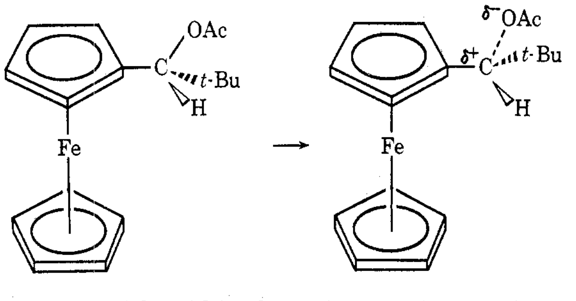
(9) J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 1295 (1965).

(10) S. H. Liggero, J. J. Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Horn, *J. Amer. Chem. Soc.*, **92**, 3789 (1970).



10



cenylcarbinols with acid in the series **6** > **5** > **4** > **7** can be assigned to a driving force for reaction to form less crowded intermediates,[11] and a speculative scheme for the observed products from **6** is presented in Chart I. An overall decrease in steric strain could direct formation of the observed products, even though some of the intermediates appear to be unfavorable. Such multiple rearrangements and fragmentations have ample precedent in the literature.[7,11b,c]

Experimental Section

General.—Analyses were performed by the M. I. T. Microchemical Laboratory, the Meade Microanalytical Laboratory, Amherst, Mass., or the Bernhardt Mikroanalytisches Laboratorium, Elbach über Engleskirchen, Germany. Routine infrared spectra were determined using Perkin-Elmer 137, 257, or 337 spectrophotometers and were calibrated against appropriate polystyrene bands. Hydroxyl stretching frequencies were measured with a Perkin-Elmer 621 grating spectrophotometer. Nmr spectra were measured with a Varian A-60 instrument with tetramethylsilane as an internal standard. Assignments of hydroxy peaks in carbon tetrachloride solution were confirmed by shaking with D_2O. Melting points (capillary) and boiling points are not corrected. Mass spectra were obtained using a Perkin-Elmer Hitachi RMU instrument. Ultraviolet spectra were obtained with a Perkin-Elmer 202 spectrophotometer. Thin layer chromatography (tlc) was carried out on glass plates coated with silica gel with the solvents noted.

***tert*-Butyl Ferrocenyl Ketone (1).**—Ferrocene (40.0 g, 0.213 mol) and aluminum chloride (22 g, 0.16 mol) were placed in a dry 500-ml three-necked flask under nitrogen with 250 ml of 1,2-dichloroethane. The flask was cooled in an ice–salt bath, and pivalyl chloride (18.1 g, 0.150 mol) in 160 ml of 1,2-dichloroethane was dripped in over 25 min with stirring. The mixture was stirred for 100 min more while warming to room temperature and then was poured on ice, the layers were separated, the water layer was washed three times with 1,2-dichloroethane, and the combined organic layers were washed successively with 3 *N* HCl, 5% NaOH, and saturated NaCl. The solvent was distilled away and the residue was steam distilled. The distillate contained 11.7 g of ferrocene contaminated with **1** and the residue consisted of 27.5 g of red solid (0.1 mol, 68% based on pivalyl chloride). Two recrystallizations from 95% ethanol gave 20.3 g (0.0748 mol, 49.9%) of **1**, mp 91–93° (lit.[12] mp 92°, lit.[13] mp 91.5–92.5°), and further recrystallization from pentane at −25° gave red-orange needles: mp 93.4–93.8°; ir (CCl_4) 1665 (C=O), 1112, and 1010 cm^{-1} (monosubstituted ferrocene); nmr (CCl_4) δ 1.28 (s, 9, *t*-Bu), 4.08 (s, 5, unsubstituted cyclopentadienyl), 4.30 and 4.71 (each broad singlet, 2, substituted cyclopentadienyl); mass spectrum (70 eV) *m/e* 270 (molecular ion).

In later preparations CH_2Cl_2 was used as solvent and after removal of part of the residual ferrocene by steam distillation the product was purified by chromatography on Florisil with pentane–ether solvent.

Anal. Calcd for $C_{15}H_{18}FeO$ (270.16): C, 66.69; H, 6.72; Fe, 20.67. Found: C, 66.45; H, 6.88; Fe, 20.12.

Di-*tert*-butylferrocenylcarbinol (6).—*tert*-Butyllithium solution (115 ml of 1 *M* solution in pentane, Foote Mineral Co.) was dripped into a solution of **1** (20.3 g, 0.0752 mol) in 1.2 l. of pentane in a dry 2-l. three-necked flask under nitrogen. After 4 hr of stirring, the mixture was poured on ice and extracted with 5% $NaHCO_3$ and then NaCl solution. Removal of the pentane left 22.6 g of gummy red solid which after chromatography on Florisil with pentane–benzene and recrystallization from acetone at −70° gave 11.5 g (0.044 mol, 57%) of **6**, mp 65–72°. Recrystallization from pentane at −25° gave red prisms: mp 75.4–76.3°; ir (CCl_4) 3632 and 3579 cm^{-1} (OH); nmr (CCl_4) δ 1.11 (s, 18, *t*-Bu's), 1.48 (s, 1, OH), and 4.1 (m, 9, aromatic H); mass spectrum (70 eV) *m/e* 328 (molecular ion).

Anal. Calcd for $C_{19}H_{28}FeO$ (328.28): C, 69.52; H, 8.60; Fe, 17.01. Found: C, 69.66; H, 8.21; Fe, 17.32.

The later chromatography fractions of this preparation gave yellow solid which was recrystallized from acetone at −70° to give 0.54 g (0.002 mol, 3%) of *tert*-butylferrocenylcarbinol (**2**) as small yellow prisms: mp 89.1–90.2° (lit.[6b] mp 90°); ir (CCl_4) 3579 cm^{-1} (OH) (lit.[6b] ir 3631.5, 3582.8 cm^{-1}); nmr (CCl_4) δ 0.83 (s, 9, *t*-Bu), 1.78 (s, 1, OH), 3.93 (s, 1, HCO), and 4.1 (m, 9, aromatic); mass spectrum (70 eV) *m/e* 272 (molecular ion).

Anal. Calcd for $C_{15}H_{20}FeO$ (272.18): C, 66.19; H, 7.41; Fe, 20.52. Found: C, 66.56; H, 7.50; Fe, 20.10.

The reduction of **1** with $NaBH_4$ also gave **2**.

Preparation of Other Tertiary Ferrocenylcarbinols.—The tertiary alcohols derived from the addition of methyl, ethyl, isopropyl, and neopentyl groups to **1** were prepared in a manner similar to that above except that in these cases a solution of **1** in ether or pentane was added to excess alkyllithium in the same solvent in the flask in which it had been prepared. Alkyllithiums were prepared from methyl iodide and ethyl bromide in ether, and isopropyl and neopentyl chlorides in pentane.

Methyl-*tert*-butylferrocenylcarbinol (3) was obtained in 85% yield after one recrystallization from pentane. Chromatography on Florisil with pentane–ether and final recrystallization from hexane at −25° gave mustard-yellow crystals: mp 92–94° (lit.[13] mp 93.5–94°); ir (CCl_4) 3581 cm^{-1} (OH); nmr (CCl_4) δ 0.81 (s, 9, *t*-Bu), 1.52 (s, 3, Me), 1.70 (s, 1, OH), and 4.1 (m, 9, aromatic); mass spectrum (70 eV) *m/e* 286 (molecular ion).

Anal. Calcd for $C_{16}H_{22}FeO$ (286.20): C, 67.15; H, 7.75; Fe, 19.51. Found: C, 67.65; H, 7.75; Fe, 20.11.

Ethyl-*tert*-butylferrocenylcarbinol (4) was obtained in 80% yield after one recrystallization from pentane at −70° and recrystallization from hexane at −25° gave brown-orange prisms: mp 85.2–87.0°; ir (CCl_4) 3573 cm^{-1} (OH); nmr (CCl_4) δ 0.82 (s, 9, *t*-Bu), 1.18 (t, 3, *J* = 8 Hz, Me), 1.52 (s, 1, OH), 2.06 (quartet, 2, *J* = 8 Hz, CH_2), and 4.1 (m, 9, aromatic); mass spectrum (70 eV) *m/e* 300 (molecular ion).

Anal. Calcd for $C_{17}H_{24}FeO$ (300.23): C, 68.01; H, 8.06; Fe, 18.60. Found: C, 68.28; H, 8.14; Fe, 19.05.

Isopropyl-*tert*-butylferrocenylcarbinol (5) was obtained in 45% yield after one recrystallization from pentane at −70°, and recrystallization from hexane at −25° gave brown-orange prisms: mp 76.8–79.1°; ir (CCl_4) 3573 cm^{-1} (OH); nmr (CCl_4) 0.86 and 1.14 (each d, 3, *J* = 8 Hz, diastereotopic methyls of isopropyl), 1.04 (s, 9, *t*-Bu), 1.87 (s, 1, OH), 2.5 (m, 1, *J* = 8 Hz, CH), and 4.1 (m, 9, aromatic); mass spectrum (70 eV) *m/e* 314 (molecular ion).

Anal. Calcd for $C_{18}H_{26}FeO$ (314.26): C, 68.79; H, 8.34; Fe, 17.77. Found: C, 68.71; H, 8.29; Fe, 17.81.

***tert*-Butylneopentylferrocenylcarbinol (7)** was obtained in 56% yield after chromatography of the initially obtained red-black oil on Florisil with pentane–ether and one recrystallization from pentane. Recrystallization from pentane at −25° gave brown-orange prisms: mp 90.2–92.3°; ir (CCl_4) 3574 cm^{-1} (OH); nmr (CCl_4) δ 0.86 and 1.13 (each s, 9, *t*-Bu), 1.54 (s, 1, OH), 1.92 (s, 2, CH_2), and 4.1 (m, 9, aromatic).

Anal. Calcd for $C_{20}H_{30}FeO$ (342.30): C, 70.17; H, 8.83; Fe, 16.32. Found: C, 69.93; H, 8.51; Fe, 16.52.

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tert-Butylferrocenylcarbinyl acetate (10) was obtained by refluxing 1.0 g of **2** with 5 ml of pyridine and 2 ml of acetic anhydride overnight and then removing the solvent at 0.1 Torr. Sublimation of the black solid at 125° (0.15 mm) yielded **10** (0.91 g, 78%), which after recrystallization from pentane at −70° was small yellow crystals: mp 90.8–93.0°; ir (CCl$_4$) 1725 cm^{-1} (C=O); nmr (CCl$_4$) δ 0.79 (s, 9, *t*-Bu), 2.17 (s, 3, Me), 4.00 (m, 9, aromatic), and 5.50 (s, 1, HCO); mass spectrum (70 eV) *m/e* 314 (molecular ion).

Anal. Calcd for $C_{17}H_{22}FeO$ (314.22): C, 64.98; H, 7.06; Fe, 17.78. Found: C, 65.09; H, 7.01; Fe, 17.65.

Methylisopropylferrocenylcarbinol (8).—Acetylferrocene (2.0 g, 0.0088 mol) in 50 ml of ether was added to the Grignard reagent prepared from isopropyl bromide (12.5 g, 0.10 mol) and Mg (5 g, 0.2 g-atom) in 150 ml of ether. The solution was refluxed for 30 min, and worked up with aqueous sulfuric acid. The solvent was removed to give a 0.80 g of red oil (40% yield based on **8**).

Chromatography on alumina with pentane–ether gave two fractions, the first being methylisopropylferrocenylcarbinol (**8**) as a red oil: ir (CCl$_4$) 3560 cm^{-1} (OH); nmr (CCl$_4$) δ 0.64 and 0.82 (each d, 3, J = 6.5 Hz, diastereotopic Me's of *i*-Pr), 1.38 (s, 3, MeCO), 1.75 (s, 1, OH), 1.4 (m, 1, -CH-*i*-Pr), 3.88 and 4.00 (each t, 2, J = 1.5 Hz, substituted cyclopentadienyl), and 4.08 (s, 5, unsubstituted cyclopentadienyl); mass spectrum (70 eV) *m/e* 254 (molecular ion minus water).

This compound was converted to the solid olefin **16** for analysis (*vide infra*).

The second fraction, after sublimation at 120° (0.1 Torr) and recrystallization from pentane, was identical with authentic 1,3-diferrocenylbut-2-en-1-one (**9**):[14] nmr (CCl$_4$) δ 2.46 (d, 3, J = 1 Hz, Me), 4.06 and 4.08 (each s, 5, unsubstituted cyclopentadienyls), 4.2–4.7 (m, 8, substituted cyclopentadienyls), 6.54 (m, 1, vinyl H).

Distillation of methylisopropylferrocenylcarbinol (**8**) at 100° (0.1 Torr) gave **2-ferrocenyl-3-methyl-2-butene (16)**, which after sublimation at 100° (0.1 Torr) was an orange solid: mp 46–48.5°; uv max (cyclohexane) 271 nm (ϵ 9100); nmr (CCl$_4$) δ 1.69 (br s, 6, =CMe$_2$), 1.98 (br s, 3, FcMeC=), 3.97 (s, 5, unsubstituted cyclopentadienyl), 3.9–4.1 (m, 4, substituted cyclopentadienyl) (weak absorptions at δ 1.08, 1.20, and 5.1 suggested the presence of <5% of the isomeric 1-isopropyl-1-ferrocenylethylene); mass spectrum (70 eV) *m/e* 254 (molecular ion).

Anal. Calcd for $C_{15}H_{18}Fe$ (254.16): C, 70.88; H, 7.14; Fe, 21.97. Found: C, 71.09; H, 7.41; Fe, 21.53.

Reaction of Di-_tert_-butylferrocenylcarbinol (6) in Acid.—A solution of **6** (0.70 g, 0.0021 mol) in 5 ml of acetic acid was added to 20 ml of 0.07 *M* perchloric acid solution (prepared by mixing 70% perchloric acid and acetic acid) with rapid stirring. The solution blackened immediately, and, after stirring for 1 min, was poured into excess NaHCO$_3$ solution and extracted twice with pentane. The pentane layer was washed with NaCl solution and evaporated, leaving a red oil which was chromatographed on silica gel with benzene to give three fractions. The first was 0.425 g (0.00137 mol, 65%) of a red oil identified as **2-ferrocenyl-3,3,4,4-tetramethyl-1-pentene (13)**: ir (CCl$_4$) 1610 (C=C), 1410 (triptyl[15]), and 905 cm^{-1} (C=CH$_2$); uv (cyclohexane) 272 nm (ϵ 8350); nmr (CCl$_4$) δ 0.83 (s, 9, *t*-Bu), 1.09 (s, 6, *t*-BuCMe$_2$), 3.91 and 4.13 (each t, 2, J = 1.5 Hz, substituted cyclopentadienyl), 3.96 (s, 5, unsubstituted cyclopentadienyl), 5.18 and 5.86 (each d, 1, J = 2 Hz, vinyl H); mass spectrum (70 eV) *m/e* 310 (molecular ion).

Hydrogenation of **13** (PtO$_2$ in acetic acid, 54 psi, 25°) and purification of the product by preparative tlc (benzene) gave **2,2,3,3-tetramethyl-4-ferrocenylpentane (15)** as a red oil: ir (CCl$_4$) 1410 cm^{-1} (triptyl[15]); nmr (CCl$_4$) δ 0.50 and 0.68 (each s, 3, diastereotopic Me's of -CMe$_2$-*t*-Bu), 0.88 (s, 9, *t*-Bu), 1.42 (d, 3, J = 7 Hz, CHMe), 2.46 (quartet, 1, J = 7 Hz, CHMe), 3.96 (s, 5, unsubstituted cyclopentadienyl), 3.8–4.0 (m, 4, substituted cyclopentadienyl); mass spectrum (70 eV) *m/e* 312 (molecular ion).

The second fraction from the chromatography of the reaction mixture from **6** was identified as **8** (0.091 g, 0.00033 mol, 16%) by comparison with the authentic material described above. The third fraction was identified as **14** (0.005 g, 1%) by comparison with authentic material prepared from acetylferrocene and methyllithium.

Preparative tlc of the reaction product from **6** with benzene gave R_f values for **13**, **14**, and **8** of 0.82, 0.47, and 0.14, respectively.

Reaction of Isopropyl-_tert_-butylferrocenylcarbinol (5) with Acid.—Under the conditions at which **6** (above) completely reacted in 1 min, **5** showed a slower conversion to a mixture of products. Thus at reaction times of 30 sec, 3 min, and 30 min there was recovered (by column chromatography on Florisil with pentane and ether–pentane mixtures) 75, 53, and 0% of starting material. The product was not identified but was apparently a mixture of olefins. The ir spectrum showed a C=C stretch at 1625 cm^{-1} and a terminal =CH$_2$ at 894 cm^{-1}, and the nmr also showed a vinyl methylene group (doublets, J = 2 Hz, at δ 5.1 and 5.6).

Reaction of Ethyl-_tert_-butylferrocenylcarbinol (4) with Perchloric Acid.—Treatment of **4** as above for 35 min and separation by column chromatography gave 20% recovered starting material and 68% of a red oil tentatively identified as 1-*tert*-butyl-1-ferrocenylpropene-1 (**11**): ir (CCl$_4$) 1625 cm^{-1} (C=C); nmr (CCl$_4$) δ 1.18 (s, 9, *t*-Bu), 1.81 (d, 3, J = 7.5 Hz, =CHMe), 4.0 (m, 9, ferrocenyl), 5.62 (q, 1, J = 7.5 Hz, =CHMe).

Reaction of _tert_-Butylneopentylferrocenylcarbinol (7) with Perchloric Acid.—Treatment of **7** as above for 30 min and separation by column chromatography gave 51% recovered starting material and 18% of a red solid identified as 1,2-di-*tert*-butylferrocenylethylene (**12**). Recrystallization from pentane at −25° gave red prisms: mp 95.2–95.8°; ir (CCl$_4$) 1580 cm^{-1} (C=C); nmr (CCl$_4$) δ 0.66 (s, 9, *t*-Bu), 1.61 (s, 9, *t*-Bu), 3.87 and 4.18 (each t, 2, J = 1.5 Hz, substituted cyclopentadienyl), 4.06 (s, 5, unsubstituted cyclopentadienyl), 5.47 (s, 1, =CH–).

Anal. Calcd for $C_{20}H_{28}Fe$ (324.29): C, 74.07; H, 8.70; Fe, 17.22. Found: C, 74.23; H, 8.73; Fe, 16.73.

Kinetics of Hydrolysis of _tert_-Butylferrocenylcarbinyl Acetate (10).—In a typical experiment 1.180 g (0.0038 mol) of **10** was dissolved in 75 ml of purified[16] acetone and 6 ml of aliquots of this material were added to each of 12 tubes containing 4 ml of water, which were then sealed. The tubes were placed on a constant-temperature bath at the appropriate temperature and agitated for 5 min while the acetate dissolved and the temperature equilibrated. Then a tube was removed for time zero, and others were removed at appropriate intervals. Liberated acetic acid was titrated to a phenol red end point with 0.1 *N* NaOH. The reactions gave reasonably good linear rate plots for 1–2 half-lives, although there was slight upward drift at long reaction times, particularly at the higher temperatures. This phenomenon is presumably due to reversal of the reaction from the dissociated ion or the carbinol. Such external return is a common feature in the reactions of α-ferrocenyl cations.[4h,17] At least two runs were made at each temperature, with a maximum deviation of ±7%.

Attempted Preparation of Methyl-_tert_-butylferrocenylcarbinyl Acetate.—A solution of methyllithium (0.014 mol) in ether was added to *tert*-butyl ferrocenyl ketone (**1**) (3.15 g, 0.012 mol) in refluxing ether, and then acetyl chloride (0.77 g, 0.0098 mol) was added. The solution was refluxed for 30 min and then evaporated, with successive removal of the precipitated white solid. The residue was chromatographed on Florisil with ether–pentane to give successively 1.38 g (44%) of material tentatively identified as **1-_tert_-butyl-1-ferrocenylethylene (21)**, 0.79 g (24%) of **3**, and 0.37 g (12%) of **1**. Purification of **21** by further chromatography gave a mobile red oil with the expected spectral properties but a poor analysis: ir (CCl$_4$) 1634 cm^{-1} (C=C); uv max (MeOH) 274 nm (ϵ 4,000); nmr (CCl$_4$) δ 1.12 (s, 9, *t*-Bu), 4.1 (m, 9, aromatic), and 5.28 and 5.66 (each d, 1, J = 2 Hz, =CH$_2$).

Anal. Calcd for $C_{16}H_{20}Fe$ (268.19): C, 71.86; H, 7.46; Fe, 20.67. Found: C, 72.72; H, 7.74; Fe, 19.71.

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