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STUDIES ON SOME FERROCENYL KETONES AND PINACOLS*

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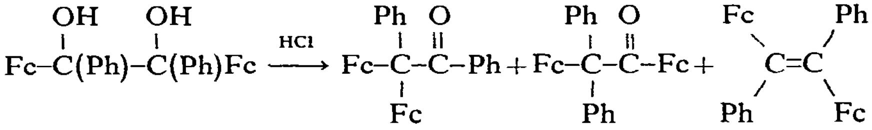
SUMMARY

The pinacol rearrangement of 1,2-diphenyl-1,2-diferrocenylethanediol produces pinacolones resulting from both phenyl and ferrocenyl group migration. The phenyl migration product, ferrocenoyldiphenylferrocenylmethane, has been converted to diphenylferrocenylmethane and ferrocenoic acid. Reduction of pivaloylferrocene with methylmagnesium bromide and cobalt chloride produces tert-butylferrocenylmethanol rather than a bimolecular product, while reduction with magnesium and magnesium iodide gives 1,2-di-tert-butyl-1,2-diferrocenylethene in good yield. The latter undergoes reduction with sodium in ethanol to form 2,2,5,5-tetramethyl-3,4-diferrocenylhexane.

Weliky and Gould[1] have described the reduction of benzoylferrocene under a variety of conditions. 1,2-Diphenyl-1,2-diferrocenylethanediol (I) could be isolated from a reduction procedure involving methylmagnesium bromide together with cobalt(II) chloride. Pinacol (I) was found to rearrange with remarkable ease in the presence of hydrogen chloride to give a pinacolone (II) resulting from migration of a ferrocenyl group.



(I) (II) (III) (VI)

We have carried out the pinacol rearrangement of (I) on a considerably larger scale than that used by Weliky and Gould. We observed that while pinacolone (II) was indeed the major rearrangement product, a smaller amount of the product from phenyl group migration (III) was also formed. The structure of (III) was supported by its cleavage under basic conditions to form, after acidification, ferrocenoic acid (IV) and diphenylferrocenylmethane (V). The ratio of ferrocenyl to phenyl group rearrangement products [(II)/(III)] was approximately 9/1 in several runs. Benzoylferrocene as

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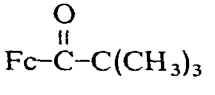
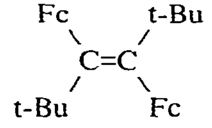
well as a very small amount of *trans*-1,2-diphenyl-1,2-diferrocenylethene (VI)[2,*] were also isolated from the rearrangement reaction. These same products, however, could be obtained simply by chromatography of a solution of pinacol (I) on alumina in the absence of hydrogen chloride. Goldberg and Bailey independently reported the isolation of both diasteriomeric forms of pinacol (I) from the Clemmensen reduction of benzoylferrocene. They further observed that each diasteriomer undergoes both ferrocenyl and phenyl group migration under acidic conditions[3,4].

In contrast to the reduction of benzoylferrocene, treatment of pivaloylferrocene (VII) with methylmagnesium bromide and cobalt(II) chloride produced, surprisingly, ferrocene together with a low yield of the Grignard addition product, tert-butylferrocenylmethylmethanol (VIII). Carbinol (VIII) has been previously mentioned in the synthesis of methyl-tert-butylcarbinylferrocene[5], although no physical properties have been reported. Further, reduction of (VII) with the binary mixture magnesium/magnesium iodide produced 1,2-di-tert-butyl-1,2-diferrocenylethene (IX) in 63% yield. By analogy with (VI) and for steric reasons, this alkene is tentatively assigned as the *trans*-isomer. Pinacol (X) is a likely intermediate in this reaction, although it was not isolated. It should be noted that small amounts of (VI) have been isolated from the magnesium/magnesium iodide reduction of benzoylferrocene[6], but that the formation of unsaturated bimolecular reduction products using this reducing agent has seldom been observed previously[7-9].



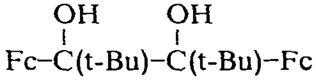
$$\mathrm{Fc{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}C(CH_3)_3}$$

(VII)



$$\mathrm{(Fc)(t\text{-}Bu)C{=}C(t\text{-}Bu)(Fc)}$$

(IX)



$$\mathrm{Fc{-}}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{(t\text{-}Bu){-}}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{(t\text{-}Bu){-}Fc}$$

(X)

As in the case of (VI)[10], treatment of alkene (IX) with an excess of sodium in ethanol readily converted it into the corresponding saturated hydrocarbon, 2,2,5,5-tetramethyl-3,4-diferrocenylhexane (XI).

EXPERIMENTAL

Proton NMR spectra were recorded on a Varian A-60 spectrometer, and infrared spectra on a Beckman IR-5 spectrometer. Melting points are uncorrected. Ethyl ether and tetrahydrofuran were purified by distillation from sodium. 1,2-Diphenyl-1,2-diferrocenylethanediol (I) was prepared in 62% yield as a yellow powder, m.p. 125–140° (reported[1] m.p. 125–145° dec.), by the reduction of benzoylferrocene with methylmagnesium bromide and cobalt(II) chloride[1]. Higher yields of (I) were obtained by employing a larger excess of Grignard reagent and a smaller volume of solvent than the amounts previously specified[1]. Pivaloylferrocene (VII) was prepared in 64% yield from a reaction between equimolar amounts of ferrocene, pivaloyl chloride, and aluminum chloride in methylene chloride solution. The product was isolated as orange needles, m.p. 91.5–92.5° (reported[11] m.p. 92°), by recrystallization of the crude product from hexane.

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[*] The *trans*-configuration of (VI) has been conclusively established[3].

Rearrangement of 1,2-diphenyl-1,2-diferrocenylethanediol (I)

A sample of 4.0 g (7 mmoles) of 1,2-diphenyl-1,2-diferrocenylethanediol (I) was dissolved in 150 ml of dry, deaerated benzene. Dry hydrogen chloride was bubbled into the solution for ca. 5 min, and the flask was stoppered and allowed to stand for 3 days. The solvent was removed under reduced pressure and the oily green residue was extracted with small portions of benzene/hexane. The extracts were chromatographed on alumina. The first band, eluted with hexane, yielded a trace amount of a yellow oil which was not identified further. A second band, eluted with benzene/hexane, produced 72 mg of 1,2-diphenyl-1,2-diferrocenylethene (VI), which was shown to be identical to an authentic sample (*vide infra*).

Elution of a third band with benzene/hexane gave 705 mg (18%) of a yellow-orange solid, which on recrystallization from benzene/ethyl ether produced yellow needles of benzoyldiferrocenylphenylmethane (II), m.p. 209–211° (N_2) (reported[1] m.p. 211° dec.). Elution of a fourth band resulted in 105 mg (2.7%) of a crystalline solid, which on recrystallization from benzene/ethyl ether gave orange-red crystals of ferrocenoyldiphenylferrocenylmethane (III), m.p. 250–251° (reported[4] m.p. 245–246° dec.). (Found: C, 72.56; H, 4.87; mol. wt. by osmometry, 550. $C_{34}H_{28}Fe_2O$ calcd.: C, 72.34; H, 5.01%; mol. wt., 564.) A KBr pellet of (III) exhibited an infrared spectrum with carbonyl absorption at 1660 cm^{-1}, phenyl absorption at 1486, 1583, and 1596 cm^{-1}, and absorption of unsubstituted cyclopentadienyl rings at 1105 and 1002 cm^{-1}. A fifth band, eluted with benzene/ethyl ether, yielded 2.5 g of benzoylferrocene, m.p. 104–106°.

Column chromatography of solutions of pinacol (I) obtained by the methylmagnesium bromide and cobalt(II) chloride reduction procedure produced benzoylferrocene in ca. 90% yield. Two very small bands were eluted before the ketone. The first band consisted of a yellow oil which turned brown rapidly after elution, and was not identified further. The second band contained a very small amount of an orange residue, which on recrystallization from benzene/ethyl ether gave orange crystals of (VI), m.p. 277–278° (N_2) (reported[10] m.p. 278–280°). The yield of (VI) was 3–5%. The product was further identified as (VI) by a total elemental analysis, a comparison of infrared and NMR spectra with those of authentic (VI)[2,10], and by a mixture melting point determination with an authentic sample.

Hydrolysis of ferrocenoyldiphenylferrocenylmethane (III)

A 75 mg sample of (III) was dissolved in 2 ml of benzene. Concentrated alcoholic potassium hydroxide solution (15 ml) was added and the reaction mixture was heated at reflux for 36 h. The mixture was concentrated to ca. 5 ml and a large excess of water was added. The mixture was filtered, and the filtrate was reduced to a small volume and subsequently extracted with several small portions of ether. The ether extracts were shaken with dilute sodium bicarbonate soln. The material remaining in the ether layer was combined with the residue from the filtration, and the aqueous layer was combined with the basic solution from the first extraction. The combined aqueous portion was acidified with hydrochloric acid, and the resulting precipitate (IV) was filtered. The precipitate was esterified in ethanol containing a drop of hydrochloric acid. The product was shown to be ethyl ferrocenecarboxylate by a comparison of its infrared spectrum with that of an authentic sample, and by a TLC comparison with the authentic ester.

The residue from the first filtration was dissolved in hexane and chromatographed on alumina. The first band, eluted with hexane, yielded ca. 25 mg of a yellow solid, which on recrystallization from methanol/water gave yellow needles of diphenylferrocenylmethane (V), m.p. 81.5–82°. A mixture m.p. of this product with an authentic sample of (V) (*vide infra*) showed no depression. A second band was eluted with hexane/benzene and was found to contain pinacolone (III).

Diphenylferrocenylmethane (V)

A solution of 0.18 g (0.49 mmole) of diphenylferrocenylmethanol in 40 ml of ethyl ether was added to a mixture of 0.66 g (5.0 mmoles) of aluminum chloride and 0.19 g (5.0 mmoles) of lithium aluminum hydride in 15 ml of ethyl ether. After the reaction mixture had been stirred for 15 min, methanol was added to destroy the excess reducing agent and the mixture was poured into a large excess of water. The ether layer was separated, dried, and the solvent was removed. Chromatography of the product on alumina gave a single yellow band which was eluted with hexane. Recrystallization of the solid from water yielded yellow crystals of (V), m.p. 81.5–82°. (Found: C, 78.65; H, 5.87. $C_{23}H_{20}Fe$ calcd.: C, 78.43; H, 5.73%.) An NMR spectrum (CS_2 soln.) of (V) exhibited a broadened singlet at τ 6.12 (unsubstituted cyclopentadienyl ring protons), a multiplet at τ 5.95 (substituted cyclopentadienyl ring protons), a singlet at τ 4.93 (methine proton), and a broadened singlet at τ 2.95 (phenyl protons). The ratio of area intensities was 7/2/1/10, respectively, and indicates that a second resonance due to unsubstituted cyclopentadienyl ring protons is hidden under the singlet at τ 6.12.

Reduction of pivaloylferrocene (VII) with methylmagnesium bromide and cobalt(II) chloride

A solution of methylmagnesium bromide (0.06 mole) in ethyl ether was cooled to 0° under nitrogen, and 0.10 g of anhyd. cobalt(II) chloride was added. To the resulting dark solution was added 5.4 g (20 mmoles) of pivaloylferrocene (VII) in 25 ml of benzene. The solution was heated to reflux for 2 h, then cooled and hydrolyzed with aqueous ammonium chloride solution. The organic layer became bright yellow after hydrolysis, while the aqueous layer contained large amounts of a dark solid. The organic phase was washed with several portions of water and was dried over anhyd. sodium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on alumina. The first band, eluted with hexane, yielded 190 mg of of an oily yellow solid. Recrystallization from hexane gave yellow crystals, m.p. 171–173°, identified as ferrocene. The second band yielded yellow crystals of m.p. 80–83°. Recrystallization from hexane afforded 270 mg (9.5%) of tert-butylferrocenylmethylmethanol (VIII), m.p. 93.5–94°. (Found: C, 67.39; H, 7.79; Fe, 19.36. $C_{16}H_{22}Fe_2O$ calcd.: C, 67.11; H, 7.76; Fe, 19.52%.) An infrared spectrum (CS_2 soln.) of (VIII) displays hydroxyl absorption at 3500 cm^{-1}, aliphatic C–H absorption as a strong band at 2940 cm^{-1}, and absorption of an unsubstituted cyclopentadienyl ring at 1106 and 1005 cm^{-1}. An NMR spectrum ($CDCl_3$ soln.) of (VIII) exhibits multiplet absorption centered at τ 5.80 (9 H, cyclopentadienyl protons), a singlet at τ 8.00 (1 H, hydroxyl proton), a singlet at τ 8.40 (3 H, methyl protons), and a singlet at τ 9.13 (9 H, tert-butyl protons). The singlet at τ 8.00 disappeared when the soln. was shaken with deuterium oxide, thus confirming its assignment.

Reduction of pivaloylferrocene (VII) with magnesium and magnesium iodide

To 2.4 g (0.10 g-atoms) of magnesium (previously activated with ethyl bromide in ethyl ether) in 10 ml of dry benzene and 50 ml of dry ethyl ether under nitrogen was added 7.5 g (0.030 mole) of iodine in small portions. Gentle heating was required initially to start the reaction. After the addition of iodine was complete, the mixture was stirred until the solution was clear and colorless. Pivaloylferrocene (6.0 g, 0.022 mole) subsequently was added; a brilliant red-purple color developed immediately. As the mixture was refluxed gently, the color gradually changed to bright red. After a 2 h reflux period, the reaction mixture was allowed to cool and was cautiously hydrolyzed with satd. ammonium chloride. Benzene (400 ml) was added to dissolve the red crystals which had formed, and the organic portion was washed with water and dried over anhyd. sodium sulfate. The volume of benzene was considerably reduced and hexane was added to the warm solution. After cooling and filtration, 3.5 g (63%) of 1,2-di-tert-butyl-1,2-diferrocenylethene (IX), m.p. 242–243° (N_2), was isolated as red crystals. (Found: C, 71.15; H, 7.36; Fe, 21.70. $C_{30}H_{36}Fe_2$ calcd.: C, 70.91; H, 7.09; Fe, 21.99%.) An infrared spectrum (KBr pellet) of (IX) exhibited no hydroxyl or carbonyl absorption. An NMR spectrum ($CDCl_3$ soln.) exhibited a sharp singlet at τ 8.90 (tert-butyl protons), a singlet at τ 5.84 (unsubstituted cyclopentadienyl ring protons), and apparent triplets at τ 5.67 and τ 5.99 (substituted cyclopentadienyl ring protons). The intensity of the singlet at τ 8.90 is equal to the total intensities of the other absorptions.

2,2,5,5-*Tetramethyl*-3,4-*diferrocenylhexane* (*XI*)

To a solution of 0.5 g (0.001 mole) of 1,2-di-tert-butyl-1,2-diferrocenylethene (IX) in 20 ml of benzene and 250 ml of absolute ethanol was added slowly 15 g (0.65 mole) of sodium cut into small pieces. The solution was heated at reflux until all the sodium had been consumed, then cooled and poured into a large excess of water. The aqueous solution was extracted with benzene and the extracts were dried over anhyd. sodium sulfate. Evaporation of the solvent and chromatography of the residue on alumina produced a broad yellow band. Removal of the solvent from this band and recrystallization of the resulting solid from hexane produced yellow crystals of (XI), m.p. 149–151°. (Found: C, 70.39; H,7.67; Fe, 21.57. $C_{30}H_{38}Fe_2$ calcd.: C, 70.59; H, 7.51; Fe, 21.50%.) An NMR spectrum ($CDCl_3$ soln.) of (XI) exhibited a sharp singlet at τ 8.68 (tert-butyl protons), a singlet at τ 6.97 (methine protons), a singlet at τ 6.00 (unsubstituted cyclopentadienyl ring protons), and a broad multiplet centered at τ 6.11 (substituted cyclopentadienyl ring protons). The absorptions at τ 6.00 and 6.11 have a combined intensity of 9, equal to that of the singlet at τ 8.68, and compared to an intensity of 1 for the singlet at τ 6.97.

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