The Clemmensen Reduction of Benzoylferrocene[1]

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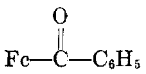
The reduction of benzoylferrocene (**1**) under conditions of the Clemmensen reduction has been described by several groups of investigators. Rausch, Vogel, and Rosenberg[3] obtained variable yields of the "normal" Clemmensen product, benzylferrocene (**2**), together with appreciable amounts of an orange-red, high-melting solid which appeared to contain only carbon, hydrogen, and iron, and which was not further identified at that time. Weliky and Gould[4] treated benzoylferrocene with ethanolic hydrogen chloride in the presence of amalgamated zinc and isolated benzoyldiferrocenylphenylmethane (**3**) in 33% yield, together with an unidentified orange substance, mp 211° dec. These same workers carried out a reduction of benzoylferrocene using zinc dust mixed with acetic and hydrochloric acids and obtained a 27% yield of **2**, a small amount of pinacolone **3**, and an unidentified solid, mp 218° dec.[5] Nesmeyanov and Kritskaya[6] reported that the reduction of benzoylferrocene with a tenfold excess of zinc amalgam and a mixture (4:1) of acetic and hydrochloric acid yielded **2**, **3**, and another product, mp 267–268°, which they suggested to be 1,1-diferrocenyl-1,2-diphenylethane (**4**).

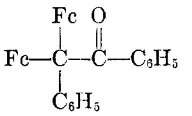


$\mathrm{Fc{-}C({=}O){-}C_6H_5}$

1

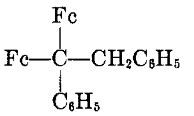
$\mathrm{Fc{-}CH_2{-}C_6H_5}$

2



$\mathrm{Fc{-}C(Fc)(C_6H_5){-}C({=}O){-}C_6H_5}$

3



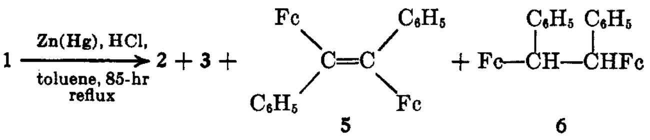
$\mathrm{Fc{-}C(Fc)(C_6H_5){-}CH_2C_6H_5}$

4

In this Note, we report the structural elucidation of the anomalous products obtained in our earlier studies on the Clemmensen reduction of benzoylferrocene.[3] A detailed study of the anomalous products obtained in the magnesium–magnesium iodide reduction of benzoylferrocene has been completed, and will be the subject of a subsequent Note.[7]

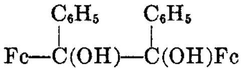
The principal product isolated in our studies has proved to be 1,2-diferrocenyl-1,2-diphenylethene (**5**) (see Scheme I). Alkene **5** was identified by its infrared and nmr spectra, by elemental analysis, and by comparison with an authentic sample prepared by the benzoylferrocene–sodium diphenylphosphinite method of Pauson and Watts (a *trans* stereochemistry for **5** was assumed by these workers).[8] The nmr spectrum of **5** is remarkable, since it exhibits a pair of apparent triplets (assigned to the A_2B_2 protons of the substituted cyclopentadienyl ring) at τ 6.05 and 6.87, both of which are upfield from the cyclopentadienyl singlet at 5.97. In many monosubstituted ferrocene derivatives, depending on the inductive and/or anisotropic effects of the substituent, both triplets are deshielded with respect to the cyclopentadienyl resonance, or one triplet appears shielded and the other deshielded with respect to this resonance. In only a few instances are *both* triplets shielded with respect to the cyclopentadienyl resonances, and in these instances the shielding effects are relatively small.[9] The appearance of both triplets, especially the one at τ 6.87, at higher field than normally found in ferrocene derivatives of a similar type may result from substantial differential shielding effects imposed by neighboring ferrocenyl or phenyl substituents, and further studies along these lines are in progress.[10]

SCHEME I



A second anomalous product isolated under our reduction conditions has been identified as the low-melting diastereomer of 1,2-diferrocenyl-1,2-diphenylethane. Alkane **6** was likewise identified by its infrared and nmr spectra, by elemental analysis, and by comparison with an authentic sample prepared by the procedure of Cais and Eisenstadt.[11] In addition to **5** and **6**, low yields of **2** and very small amounts of **3** were also obtained in several runs.

The formation of dimeric products in the Clemmensen reduction of diaryl ketones is not without precedent. For example, Steinkopf and Wolfram[12] observed that the Clemmensen reduction of benzophenone in aqueous–acidic media gave benzopinacol as the major product together with only trace amounts of diphenylmethane. An alternate reduction of benzophenone employing amalgamated zinc, dry hydrogen chloride, and ethanol produced tetraphenylethylene in 45% yield, in addition to diphenylmethane and benzopinacolone. In our studies, 1,2-diferrocenyl-1,2-diphenylethanediol (**7**)[4] is most likely an intermediate in the formation of



$\mathrm{Fc{-}C(OH)(C_6H_5){-}C(OH)(C_6H_5)Fc}$

7

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[1] (a) Part XIII of a series "Organometallic π-Complexes." Part XII: M. D. Rausch and D. J. Ciappenelli, *J. Organometal. Chem.*, in press. (b) Presented at the 2nd Middle Atlantic Regional Meeting of the American Chemical Society, New York, N. Y., Feb 1967, Abstracts of Papers, p 51.

[2] National Science Foundation Undergraduate Research Fellow, 1965 and 1966.

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

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

[5] It seems probable that the unidentified products of mp 211 and 218°, isolated by Weliky and Gould, were the low-melting diastereomer of 1,2-diferrocenyl-1,2-diphenylethane.

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

[7] M. D. Rausch and D. L. Adams, to be published.

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

[9] (a) M. D. Rausch and V. Mark, *J. Org. Chem.*, **28**, 3225 (1963); (b) M. D. Rausch, *ibid.*, **28**, 3337 (1963); (c) R. A. Benkeser, Y. Nagai, and J. Hooz, *Bull. Chem. Soc. Japan*, **36**, 482 (1963); (d) G. G. Dvoryantseva, S. L. Portnova, K. I. Grandberg, S. P. Gubin, and Yu. N. Sheinker, *Doklady Akad. Nauk SSSR*, **160**, 1075 (1965).

[10] In contrast, the nmr spectra of vinylferrocene, 1-ferrocenyl-1-phenylethene, and *trans*-1-ferrocenyl-2-phenylethene all exhibit two apparent triplets *downfield* from the cyclopentadienyl resonance peak: M. D. Rausch and A. Siegel, unpublished studies.

[11] M. Cais and A. Eisenstadt, *J. Org. Chem.*, **30**, 1148 (1965). See also references cited therein concerning previous isolations of **6** and its diastereomer. These workers have also suggested that alkane **6** was a reduction product in our earlier studies.

[12] W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923).

pinacolone **3** and may also conceivably serve as a precursor for **5** and **6**.

It is obvious from the present results and the findings of others that the Clemmenson reduction of benzoylferrocene produces a variety of products, depending on the nature of the reducing agent, the solvent used, the reaction time, etc. The reduction appears to have little synthetic value as a reliable route to benzylferrocene, since there are available much better methods employing sodium and ethanol[3] or lithium aluminum hydride–aluminum chloride.[13] The nature and mechanism of formation of the bimolecular products obtained from the Clemmensen reduction of aryl ferrocenyl ketones are of interest, however, and are under further investigation in our laboratory.

Experimental Section

General.—Benzoylferrocene was prepared according to a published procedure.[3] Elemental analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Nmr spectra were obtained in deuteriochloroform solution on a Varian A-60 spectrometer, and infrared spectra were obtained as potassium bromide pellets on a Beckman IR-10 spectrophotometer. Chromatography was generally performed on columns wrapped with aluminum foil to protect the compounds from light.

Clemmensen Reduction of Benzoylferrocene.—The yields of the various products produced in this reaction have been found to vary appreciably, and the following is given as a typical reaction procedure and work-up.

Into a 1-l. flask equipped with a mechanical stirrer and reflux condenser were placed 60 g (0.92 g atom) of zinc dust, 4.5 g (0.017 mole) of mercuric chloride, 75 ml of water, and 3.0 ml of concentrated hydrochloric acid. The mixture was heated with stirring to near reflux for 10 min, the water was then decanted, and to the resulting zinc amalgam was added 30 ml of water, 60 ml of concentrated hydrochloric acid, and 100 ml of toluene. To this mixture at reflux was added 17.4 (0.06 mole) of benzoylferrocene (**1**). The reaction mixture was then allowed to stir at reflux for 85 hr, with periodic addition of 150 ml of concentrated hydrochloric acid (25-ml portions every 12–15 hr).

The reaction mixture was allowed to cool to room temperature, filtered, and the filtered material was washed with water and hexane and was dried. There remained 4.57 g (28% yield) of 1,2-diphenyl-1,2-diferrocenylethene (**5**) in the form of an orange-red solid, mp 274–276° (N_2). Recrystallization of this solid from xylene–heptane produced a product of mp 277–278° (lit.[14] mp 278–280°); a mixture melting point determination with an authentic sample[14] showed no depression. Both infrared and nmr spectra of **5** were consistent with the proposed formulation and were identical with analogous spectra obtained from an authentic sample.[14]

The solvent was evaporated from the organic portion after washing twice with 5% sodium bicarbonate solution. The resulting solid was triturated 5–6 times with hexane and was filtered. The filtrate was evaporated to give an oily product which was chromatographed on an alumina column. The first (main) band was eluted with hexane–benzene, and the product was recrystallized from hexane to produce 1.21 g (7%) of orange-yellow crystals of benzylferrocene (**2**), mp 73–74° (lit.[15] mp 76°). The second and third bands were eluted with benzene and produced very small amounts of **6** and **3**, respectively. These products were identified by tlc and by comparison of their nmr spectra with the spectra of authentic samples.[4,11]

The insoluble material after trituration with hexane was extracted with boiling acetone. A very small amount of red solid, identified as **5**, precipitated and was filtered. Concentration of the filtrate and subsequent cooling produced 0.68 g (4% yield) of 1,2-diferrocenyl-1,2-diphenylethane (**6**), mp 218–220° (lit.[16] mp 218–220°); a mixture melting point determination with an authentic sample showed no depression. The infrared spectrum of **6** exhibited absorption peaks at 3070, 1102, 998 and 910 cm^{-1} (ferrocenyl group), 2897 cm^{-1} (aliphatic C-H), and other principal peaks at 3020, 1598, 1485, 1450, 926, 775 and 705 cm^{-1} which may be assignable to the phenyl groups. The nmr spectrum of **6** indicated a multiplet centered at τ 2.77 (10 H, phenyl protons) and a multiplet between 5.9 and 6.4 (20 H, ferrocenyl and methine protons). Both infrared and nmr spectra were identical with analogous spectra obtained from an authentic sample.[11]

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[13] K. Schlögl, A. Mohar, and M. Peterlik, *Monatsh.*, **92**, 921 (1961).

[14] P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 3880 (1962).

[15] B. F. Hallam and P. L. Pauson, *ibid.*, 3030 (1956).

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

Thermal Decomposition of *p*-Tosylhydrazones

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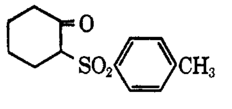
Since Bamford and Stevens[1] first described the thermal decomposition of the anions of tosylhydrazones, there has been a widespread interest in this reaction. However, pyrolysis of the parent tosylhydrazones has been considered in only one Note during this period. Lin and Just[2] reported that acetone *p*-tosylhydrazone decomposed rapidly when heated to 160° and furnished a low yield of 1-*p*-tosyl-3,5,5-trimethyl-2-pyrazoline. These investigators also examined several other tosylhydrazones, but the pyrolysis products were not characterized.

Some additional examples of the thermal decomposition of tosylhydrazones have now been noted. The results (Table I and following discussion) suggest at least three types of reaction: tosyl ketone formation; aldol condensation and/or pyrazoline formation, and sulfone formation.

Tosyl Ketone Formation.—Cyclohexanone *p*-tosylhydrazone decomposed vigorously and exothermically when heated to 145–150°; even after 12 days at 80° the crystalline hydrazone was completely converted to a dark, resinous mass. The reaction could also be effected by refluxing cyclohexanone and *p*-toluenesulfonylhydrazine in glacial acetic acid. Work-up of these reaction mixtures revealed essentially the same products, which included ammonium *p*-toluenesulfonate, *p*-toluenesulfonamide, di-*p*-tolyl disulfide, *p*-tolyl-*p*-toluenethiosulfonate, *p*-toluenesulfonylhydrazinium *p*-toluenesulfonate, together with small amounts of two compounds which still contained the cyclohexyl moiety. From the nmr and infrared spectra and the elemental analyses it was deduced that one of these compounds was a *p*-tosylcyclohexanone. That it was the 2-*p*-tosyl isomer, **1**, was proved by comparison with an authentic sample; 2,4-dinitrophenylhydrazones from both samples of tosylcyclohexanone were also identical. (The isomeric 3-*p*-tosylcyclohexanone which was also made for the purpose of comparison was different.) The other compound was the azine of the 2-*p*-tosylcyclohexanone, **2**.



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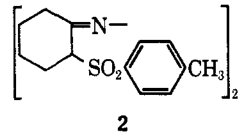

2

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[1] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

[2] Y.-C. Lin and G. Just, *Can. J. Chem.*, **43**, 3116 (1965).