bonds are broken: formation of the hydroperoxide salt and reduction of the salt.[5] The stereochemistry of the two steps apparently is the same, however.[2] The insensitivity of the product ratio to temperature is suggestive of a free-radical process for these steps. Kooyman and Vegter,[6] for example, obtained the same ratio of *exo–endo* norbornyl chlorides at both 42° and 150° in an investigation of radical-catalyzed chlorination of norbornane.

Experimental

Chromosorb P (35/80) was the solid phase used in the gas chromatographic work. The columns were $^{1}/_{4}$-in. o.d. copper tubing of the indicated lengths. Boiling points are uncorrected.

exo-**Norbornyl bromide** was prepared by addition of hydrobromic acid to norbornene[7] and had b.p. 78–80° (19 mm.) (lit.[7] b.p. 82°/29 mm.).

Preparation of the Grignard Reagent of Norbornyl Bromide.—The reagent was prepared in dried apparatus under nitrogen by addition of 5.0 g. (0.029 mole) of the bromide in 20 ml. of dry ether to 1.0 g. (0.041 g.-atom) of magnesium under 15 ml. of ether containing a crystal of iodine. The mixture was refluxed for 1 hr.

Carbonations were carried out by bubbling carbon dioxide from Dry Ice through concentrated sulfuric acid, a calcium chloride drying tower, and into the reaction flask held at 25° or −78°. The mixture was decomposed with 2 *N* hydrochloric acid and extracted with ether. The acidic products were removed by washing with potassium carbonate solution. The yields of acidic and neutral products formed at the two temperatures were as follows: 25°, 1.4 g. (35%) and 1.7 g. −78°, 0.9 g. (22%) and 2.3 g. (1 hr. carbonation); 1.0 g. (25%) and 2.3 g. (2 hr. carbonation).

Analyses of the acids were effected by conversion to methyl esters using boron trifluoride–methanol reagent[8] followed by gas chromatography. The best separation was acheived on a 10 ft. castorwax column (25%) at 142°. The curves were matched with known mixtures of the esters prepared by weighing pure samples. No noticeable epimerization took place during the esterification since the standard samples were also made with the boron trifluoride reagent. The analyses are probably accurate to ±3%. At 25° the *exo:endo* ratio was 70:30; at −78° the ratio was 90:10 in both cases.

Oxygenations were carried out in a similar manner using air in place of carbon dioxide. The reaction mixtures were decomposed with dilute sulfuric acid and extracted with ether. The alcohols were separated from the other neutral products by chromatography on "activated" alumina. Hexane was used to elute everything but the alcohols and methanol was used to remove the alcohols. The analyses were carried out by gas chromatography on an 8 ft. column of carbowax 20M (15%) at 102°. At 25° the yield of mixed norbornanols was 1.8 g. (56%) and 2.4 g. of other neutral products were obtained; the ratio of *exo* to *endo* alcohol was 79:21. At −78° there was obtained 1.9 g. (59%) of alcohols and 2.4 g. of other products; the ratio of *exo* to *endo* alcohols was 80:20. Ratios of peak areas were used to determine these percentages. It was shown that the alumina did not isomerize *exo*-norbornanol.

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(5) C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77**, 6032 (1955).

(6) E. Kooyman and G. Vegter, *Tetrahedron*, **4**, 382 (1958).

(7) J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(8) Applied Science Laboratories, Inc., State College, Pennsylvania. See L. D. Matcalfe and A. A. Schmitz, *Anal. Chem.*, **33**, 363 (1961), for procedure.

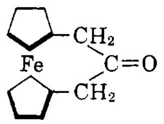
The Synthesis of Bridged Ferrocene Derivatives with Functional Groups on the β-Carbon of the Bridge[1]

William Mock and John H. Richards

Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, Pasadena, California

Received February 1, 1962

For future mechanistic studies it was desirable to have bridged ferrocene derivatives with functional groups on the β-carbon of the bridge. To this end, the dimethyl ester of ferrocene-1,1′-diacetic acid,[2] was treated with sodium triphenylmethyl in anhydrous ether. The red color of the triphenylmethyl anion soon disappeared and after work-up and chromatography there was obtained in 85% yield 1,1′-(α-carbomethoxy β-ketotrimethylene)ferrocene which was directly hydrolyzed and decarboxylated in glacial acetic acid with hydrochloric acid to 1,1′-(α-ketotrimethylene)ferrocene (I). Reduction of the ketone with sodium borohydride led to 1,1′-(β-hydroxy-trimethylene)ferrocene. The structure of the ketone was proved by desulfurization of its dimethylthioketal derivative with Raney nickel which produced the known 1,1′-trimethyleneferrocene.[3]



I

A principal point of interest in the synthesis is the ease of effecting the Dieckmann cyclization which may suggest that two of the bridging atoms can be planar with considerable double bond character between them. This is further borne out by the smooth preparation of an enol acetate derivative of 1,1′-(α-carbomethoxy-β-ketotrimethylene)ferrocene which possesses a double bond between the α- and β-carbons of the bridge. This is the first reported case of a ferrocene derivative bridged by a three-carbon chain containing a double bond.

NOTE ADDED IN PROOF: Rosenblum[4] has also recently reported bridged ferrocene derivatives with double bonds in the bridge.

A second point of interest is the carbonyl stretching frequency of 1,1′-(β-ketotrimethylene)ferrocene which occurs at 1703 cm.$^{-1}$ in carbon tetrachloride solution. This shift to lower frequencies (*cf.*

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(1) Supported in part by a grant from the NSF and from the Paint Research Institute.

(2) K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *J. Am. Chem. Soc.*, **79**, 3420 (1957).

(3) K. Schlögl and H. Seiler, *Monatsh.*, **91**, 79 (1960).

(4) M. Rosenblum, A. K. Banerjee, N. Danieli, and R. W. Fish, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962, p. 2-Q.

acetone 1719 cm.$^{-1}$) may be caused either by a slight opening of the C—CO—C bond angle to 123°[5] or by an interaction of the d-electrons of the adjacent iron atom with the π-electrons of the carbonyl groups.

Experimental

1,1'-(α-Carbomethoxy-β-ketotrimethylene)ferrocene.—To a solution of dimethyl 1,1'-ferrocenediacetate (0.22 g., 0.67 mmole) dissolved in anhydrous ether (20 ml.) was added an ethereal solution of sodium triphenylmethide (0.12 *M*). The reaction was maintained under an atmosphere of nitrogen and the addition was continued until the distinctive red color of sodium triphenylmethide persisted. An orange precipitate immediately formed. The molar ratio (methide/ester) required was 2.9 for several runs. After standing at room temperature for 4 hr., the solution was shaken with water, the orange precipitate dissolving in the ether phase. The ethereal solution was washed with water, dried over anhydrous sodium sulfate, and the ether removed. The residue was chromatographed on a silicic acid–Celite column with hexane–dichloromethane as eluent. The first band of triphenylmethane was followed by the product which was crystallized from heptane yielding 0.17 g. (85%) of orange needles, m.p. 121–121.5°.

Anal. Calcd. for $C_{15}H_{14}O_3Fe$: C, 60.41; H, 4.74; Fe, 18.74. Found: C, 60.34; H, 4.93; Fe, 18.90.

Enol Acetate of 1,1'-(α-Carbomethoxy-β-ketotrimethylene)-ferrocene.—1,1'-(α-Carbomethoxy-β-ketotrimethylene)-ferrocene (0.1 g., 0.24 mmole) was added to 20 ml. of isopropenyl acetate which contained 0.2 g. of sulfosalicylic acid as catalyst. The mixture was heated to 90° and held at that temperature for 6 hr. The solution (containing a dark red precipitate) was neutralized with sodium bicarbonate solution and then extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, and the ether removed. The residue was chromatographed on a column of silicic acid–Celite with hexane–chloroform eluent. The product was recrystallized from heptane yielding 0.06 g. (75%) of orange needles, m.p. 149–150°.

Anal. Calcd. for $C_{17}H_{16}O_4Fe$: C, 60.03; H, 4.74; Fe, 16.43. Found: C, 60.22; H, 4.91; Fe, 16.27.

1,1'-(β-Ketotrimethylene)ferrocene.—1,1'-(α-Carbomethoxy-β-ketotrimethylene)ferrocene (0.25 g., 0.84 mmole) was dissolved in a mixture of 20 ml. of glacial acetic acid and 3 ml. of concentrated hydrochloric acid. The mixture was heated at 100° for 30 min. After cooling, the solution was neutralized to pH 8 with sodium hydroxide followed by sodium bicarbonate, extracted with ether, and the ether dried over anhydrous sodium sulfate. After removing the ether, the residue was chromatographed over silicic acid–Celite with hexane–dichloromethane eluent, and the product recrystallized from heptane, yielding yellow-orange needles (0.17 g., 85%) m.p. 154–155°.

Anal. Calcd. for $C_{13}H_{12}OFe$: C, 65.01; H, 5.04; Fe, 23.28. Found: C, 65.12; H, 4.79; Fe, 23.46.

1,1'-Trimethyleneferrocene.—1,1'-(β-Ketotrimethylene)-ferrocene (52 mg. 0.22 mmole) was dissolved in 10 ml. of glacial acetic acid and 5 ml. of concentrated hydrochloric acid and 5 ml. of methyl mercaptan were added. The mixture was allowed to stand at 0° for 20 min. and was then neutralized with sodium hydroxide and extracted with ether. After removal of the ether the product was crystallized from octane, yielding 52 mg. (73%) of orange crystals, m.p. 160–162°. Without further purification, the thioketal was refluxed with W-5 Raney nickel in absolute ethanol for 3 hr. with mechanical stirring. The reaction mixture was filtered, acidified, and the product extracted with ether. The ether was evaporated and the residue chromatographed on Merck neutral alumina with hexane as eluent. A yellow solid thus was obtained which after sublimation at 2 mm. at 64° had m.p. 105–106° (lit.,[3] 105–106°). The same product was obtained by Clemmensen reduction of 1,1'-(α-ketotrimethylene)ferrocene.[6]

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[5] P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961).

[6] K. L. Rinehart, Jr., and R. J. Curby, Jr., *ibid.*, **79**, 3290 (1957).

Formation of an Organotin–Nitrogen Bond

KEIITI SISIDO AND SINPEI KOZIMA

Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

Received June 6, 1962

Tin–nitrogen bonding in triammonotin halides, $Sn(NH_2)_3X$ (where X stands for a halogen atom), are known,[1–3] but the same bonding in organotin compounds has apparently not been described as yet.

The reaction of ammonia or an amine with organotin compounds gives complex addition compounds containing one or two moles of ammonia or amine as coordinating components.[4–8]

It has been discovered that the reaction of diethylaminomagnesium bromide with trialkyltin chlorides gives trialkyl(diethylamino)tins having an organotin–nitrogen bonding (equation 1). The aminotin compounds could be isolated analytically pure by distillation under reduced pressure. The oily product reacted with hydrochloric acid to give trialkyltin chloride and the same amine hydrochloride (equation 2), both compounds being identified by the infrared spectra and the melting points. Upon exposure to air trialkyl(diethylamino)tin compounds were attacked very quickly by atmospheric moisture and carbon dioxide to afford diethylamine and trialkyltin carbonate (equation 3). The infrared spectra of triethyltin carbonate thus obtained coincided in every respect with those of the authentic sample prepared from carbon dioxide and bis(triethyltin) oxide.

$$R_3SnCl + (C_2H_5)_2NMgBr \longrightarrow R_3SnN(C_2H_5)_2 + MgBrCl \quad (1)$$

$$R_3SnN(C_2H_5)_2 + 2HCl \longrightarrow R_3SnCl + (C_2H_5)_2NH{\cdot}HCl \quad (2)$$

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[1] R. Schwalz and A. Jeanmaire, *Ber.*, **64**, 1442 (1932).

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[3] E. Bannister and G. W. A. Fowles, *ibid.*, 4374 (1958).

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[7] F. Ephraim and T. Schmidt, *Ber.*, **42**, 3856 (1909).

[8] See also R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 508 (1960), for further references.