Journal of Organometallic Chemistry, 61 (1973) 347–354

© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

1-*exo*- AND 1-*endo*-(TRIMETHYLSILYL)-2,3-FERROCENOINDENE. PREPARATION AND METHANOLYSIS IN THE PRESENCE OF FERRIC CHLORIDE

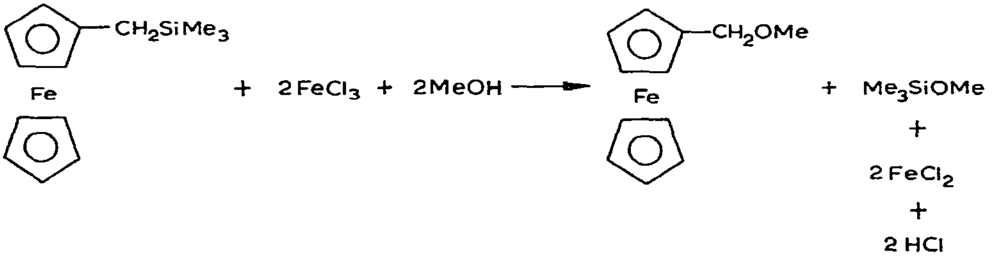
TADAO KONDO, KEIJI YAMAMOTO and MAKOTO KUMADA
Department of Synthetic Chemistry, Kyoto University, Kyoto 606 (Japan)
(Received February 16th, 1973)

SUMMARY

The reaction of 1-*endo*-methoxy-2,3-ferrocenoindene (IIb) with lithium followed by treatment with trimethylchlorosilane gave 1-*exo*-(trimethylsilyl)-2,3-ferrocenoindene (Ia) as the sole product. The latter was found to isomerize to the *endo* isomer (Ib) when treated with excess of n-butyllithium. Methanolysis of both (Ia) and (Ib) in the presence of ferric chloride gave 1-*exo*-methoxy-2,3-ferrocenoindene (IIa). The configurational identification of (Ia), (Ib), (IIa), and (IIb) was made on the basis of the ^{1}H NMR spectra.

INTRODUCTION

In a recent paper[1], we have reported a reaction of ferrocenylmethyl derivatives of silicon and germanium with methanol in the presence of ferric ions. For instance, the carbon–silicon bond of (ferrocenylmethyl)trimethylsilane readily undergoes cleavage in a methanol solution of anhydrous ferric chloride at room temperature to give ferrocenylmethyl methyl ether and methoxytrimethylsilane as shown in eqn. (1).



(1)

The results were discussed in terms of a mechanism which involves an initial formation of a substituted ferricenium ion in a redox process with ferric ions followed by nucleophilic attack of solvent methanol on the silicon atom. The resulting ferrocenylmethyl radical, though it may never be wholly free, as a leaving group is immediately oxidized by ferric ion to give a ferrocenylmethyl cation which in turn gives the observed ferrocenylmethyl methyl ether.

In an effort to provide further insight into the mechanism, we have examined a similar reaction of 1-(trimethylsilyl)-2,3-ferrocenoindene (I), because the relatively unstable behavior of 2,3-ferrocenoindenyl cation reported by Cais *et al.*[2] may emerge in the course of the solvolytic reaction of (I).

We report here the preparation and characterization of 1-*exo*- and 1-*endo*-(trimethylsilyl)-2,3-ferrocenoindene, (Ia) and (Ib), and also a stereochemical study of the methanolysis of these compounds in the presence of anhydrous ferric chloride. Some aspects of the reaction stereochemistry of an α-ferrocenyl carbanion with electrophiles, such as a proton or a trimethylsilyl group, in connection with the preparation of (Ia) and (Ib) are also described.

RESULTS AND DISCUSSION

Preparation and characterization

The preparative route is summarized in Scheme 1 and the ^1H NMR data for compounds (Ia), (Ib), (IIa), and (IIb) are listed in Table 1.

The precursors of 1-*endo*-methoxy-2,3-ferrocenoindene (IIb) were prepared

SCHEME 1

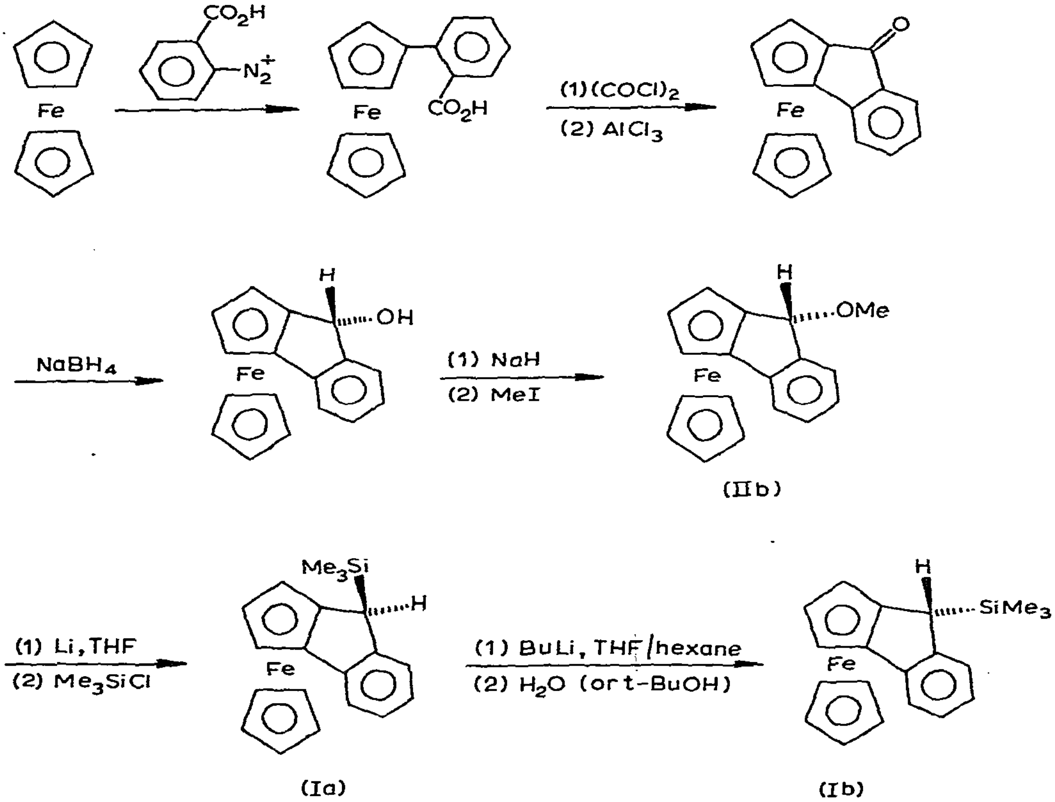


TABLE 1

^{1}H NMR DATA FOR SOME SUBSTITUTED 2,3-FERROCENOINDENES[a,b]

Compound No.	*Chemical shift* (τ)					
	$(CH_3)_3Si$	CH_3O	CH	C_5H_5	C_5H_3	C_6H_4
(Ia)	10.13 (s)		6.64 (s)	6.31 (s)	6.04–5.45 (m)	3.06–2.46 (m)
(Ib)	9.63 (s)		6.95 (s)	6.11 (s)	6.01–5.51 (m)	3.09–2.11 (m)
(IIa)		7.03 (s)	4.60 (s)	6.17 (s)	5.90–5.40 (m)	3.08–2.58 (m)
(IIb)		6.27 (s)	5.08 (s)	6.01 (s)	5.93–5.53 (m)	3.05–2.60 (m)

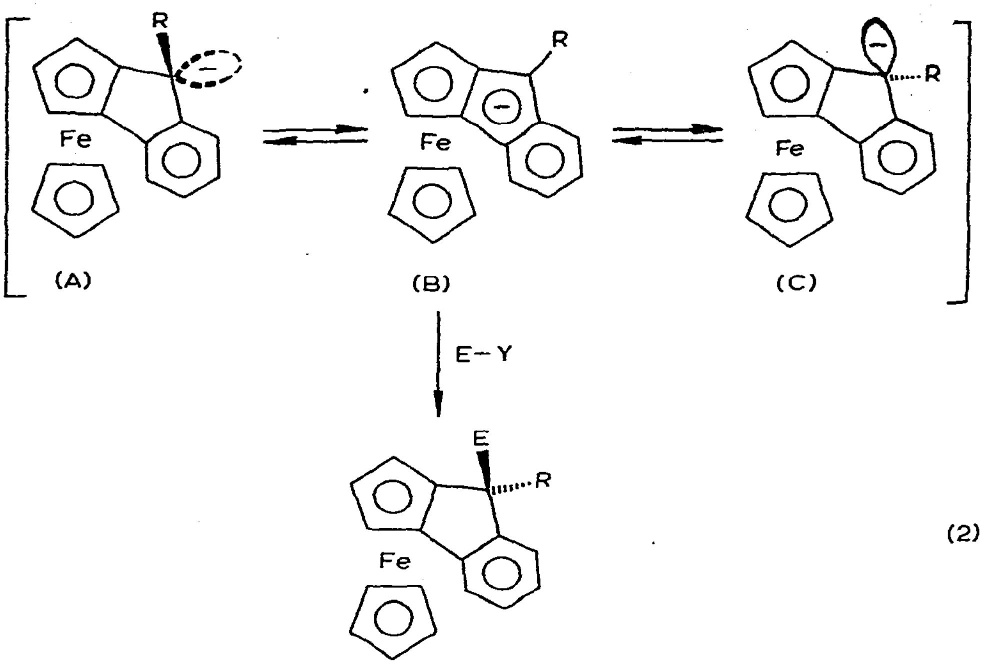
[a] Recorded on a Varian T60 spectrometer in carbon tetrachloride solution with cyclohexane or tetramethylsilane as internal standard. [b] The spectrum of 1-*endo*-hydroxy-2,3-ferrocenoindene had resonances at τ 8.17 (d, J 10.0 Hz, OH), 6.00 (s, C_5H_5), 5.83–5.43 (m, C_5H_3), 4.88 (d, J 10.0 Hz, CH), and 3.06–2.50 ppm (m, C_6H_4).

by known procedures[2–4]. (IIb) was then prepared in 34% yield from a reaction of 1-*endo*-hydroxy-2,3-ferrocenoindene with sodium hydride in tetrahydrofuran (THF) followed by treatment with methyl iodide. 1-*exo*-(Trimethylsilyl)-2,3-ferrocenoindene (Ia) was selectively obtained in 72% yield from a reaction of trimethylchlorosilane with 2,3-ferrocenoindenyllithium prepared *in situ* from (IIb) and lithium in THF in a similar manner to that used for the preparation of (ferrocenylmethyl)trimethylsilane reported by Nesmeyanov *et al.*[5].

Interestingly, (Ia) was found to isomerize completely to 1-*endo*-(trimethylsilyl)-2,3-ferrocenoindene (Ib) when (Ia) was treated with excess of n-buthyllithium in THF/hexane followed by hydrolysis or alcoholysis with tert-butyl alcohol.

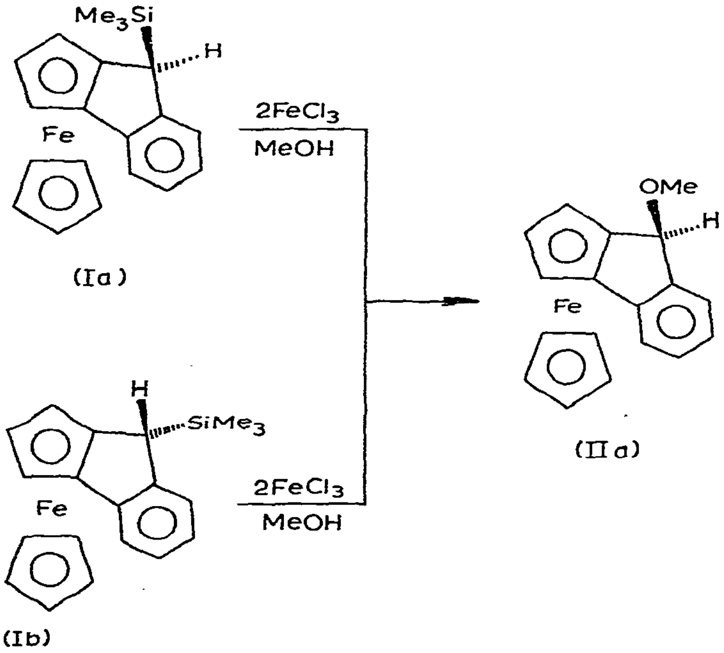
The configuration of compounds (Ia), (Ib), (IIa) (see below), and (IIb) was established by their characteristic chemical shifts in ^{1}H NMR spectra (Table 1) according to the observations of Turbitt and Watts[6], who have investigated the ^{1}H NMR spectra of a series of homoannularly bridged [3](1,2)ferrocenophane derivatives and established that *exo* substituent α-protons with respect to the cyclopentadienyl ring (*viz.* located above the plane of the ring remote from the iron atom) are more shielded compared with the protons of the same substituent in an *endo* configuration (*viz.* below the plane of the ring), although the region much closer to the iron atom is strongly shielded. The greater shielding of the methine proton of (IIb) relative to that of (IIa) (see Table 1) is consistent with the fact that methylation of 1-*endo*-hydroxy-2,3-ferrocenoindene proceeds, as expected, with retention of configuration at carbon attached to oxygen to give (IIb).

On the other hand, both conversions, (IIb)→(Ia) and (Ia)→(Ib), have been found to occur with complete inversion of configuration at carbon attached directly to the ferrocene ring. These observations show that the attack of an electrophile such as Me_3SiCl, H_2O, and t-BuOH on the 2,3-ferrocenoindenyl anions, for which (B) [or (C)] in eqn. (2) may be postulated as a preferred structure, occurs exclusively from the *exo* direction. That is product formation is largely sterically controlled, although electronic factors may also operate. Only a few studies on α-ferrocenyl carbanions, in contrast to the corresponding carbonium ions, have been reported[5,7,8] and to our knowledge this is the first stereochemical observation of the reaction of such an anion with electrophiles.



(2)

R=H or $SiMe_3$. E–Y=Me_3SiCl, H–OH, or H–O–t-Bu



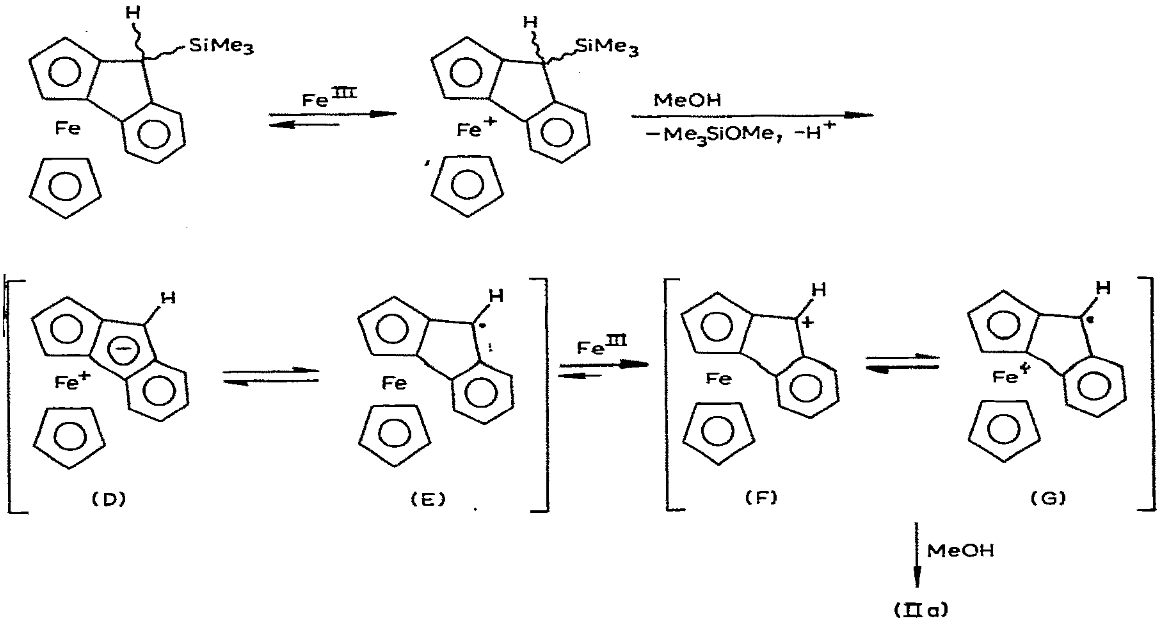
(3)

Methanolysis of (Ia) and (Ib) in the presence of anhydrous ferric chloride

It has been found that both (Ia) and (Ib) undergo readily cleavage of the C–Si bond when treated with two equivalents of anhydrous ferric chloride for each molecule of the substrate in oxygen-free absolute methanol at room temperature for 10 min and give the same product, *viz.* 1-*exo*-methoxy-2,3-ferrocenoindene (IIa) [eqn. (3)], while after many hours reaction a mixture of (IIa) and (IIb) is obtained. Qualitatively, (Ia) reacted faster than (Ib).

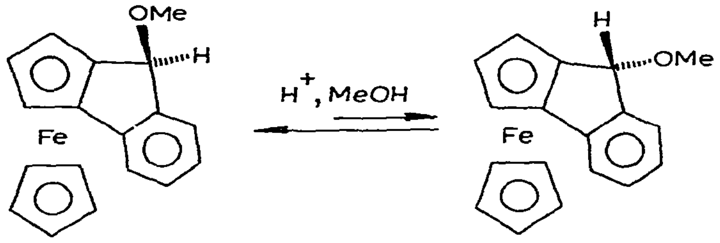
The results may be reasonably interpreted by the same mechanism as described for the reaction of *e.g.* (ferrocenylmethyl)trimethylsilane in the previous paper[1]; namely, a 2,3-ferrocenoindenyl cation intermediate (F) is involved in the product-determining step (Scheme 2). The latter may undergo nucleophilic attack by methanol from the *exo* direction. It is well established that addition of a reagent to an unsaturated carbon atom (*e.g.* carbonyl, vinylic, or cationic) attached directly to the ferrocene ring occurs predominantly, if not exclusively, from the *exo* direction[9-12].

SCHEME 2



It should be noted that no dimerization product derived from (E) or (G) was detected in these reactions which is in line with the previous observation[1] that under the conditions employed, no free radical species may be generated, whereas it has been reported by Cais *et al.*[2] that 2,3-ferrocenoindenyl cation, generated from 1-hydroxy-2,3-ferrocenoindene in the presence of fluoroboric acid in acetic anhydride, undergoes a very fast intramolecular redox process, (F)$\rightleftharpoons$(G) to give the dimerization product of (G).

Finally, the fact that a mixture of (IIa) and (IIb) was obtained in the reaction of (Ia) or (Ib) after many hours reaction would suggest that there was some epimeri-



(IIa) (IIb) (4)

zation of (Ia) and also (Ib) presumably catalyzed by hydrogen chloride formed during the reaction. Indeed, treatment of (IIa) with hydrogen chloride in oxygen-free absolute methanol (0.224 *M*) at room temperature for 46 h gives an isomeric mixture of (IIa) and (IIb) in a ratio of 2.0/1, while similar treatment of (IIb) yields an analogous mixture in a ratio of 4.0/1 after 40 h [eqn. (4)]. Although nucleophilic attack by methanol on a carbonium ion center from the *endo* direction is much more disadvantageous as mentioned above, the *endo* isomer (IIb), once formed, would accumulate because (IIb) may be expected to resist solvolysis more strongly as compared with the *exo*-isomer (IIa)[10]. Similar epimerization of 1-hydroxy-(or 1-methoxy)-2,2-dimethyl-[3](1,2)ferrocenophane has been reported by Watts *et al.*[6].

EXPERIMENTAL

All boiling and melting points are uncorrected. 1-*endo*-Hydroxy-2,3-ferrocenoindene[2,4] (m.p. 92–93°; lit. m.p. 90–91°) was prepared by reduction of 2,3-ferrocenoindenone[2-4] with sodium tetrahydroborate in a similar way to that described in the literature.

1-*endo-Methoxy-2,3-ferrocenoindene* (*IIb*)

To a mixture of 5.0 g (50% dispersion in oil, 0.10 mole) of sodium hydride in 300 ml of THF was added dropwise a solution of 7.6 g (0.026 mole) of 1-*endo*-hydroxy-2,3-ferrocenoindene in 100 ml of THF. The mixture was heated under reflux for 6 h. Methyl iodide (30 g, 0.21 mole) was then added to the mixture with cooling in an ice-bath and the mixture was refluxed for 24 h. It was then hydrolyzed and the resulting organic layer was separated. The aqueous layer was extracted with hexane and the combined organic layer was dried over anhydrous sodium sulfate. After evaporation of the solvents, the residue was chromatographed over alumina using ether as an eluant and then fractionally distilled to give 4.0 g (34% yield) of 1-*endo*-methoxy-2,3-ferrocenoindene (IIb), b.p. 132–136°/0.03 mmHg. (Found: C, 71.24; H, 5.48. $C_{18}H_{16}FeO$ calcd.: C, 71.08; H, 5.30%.) The IR spectrum (recorded on a Hitachi EPI-G3 grating spectrophotometer) indicated the presence of a methoxy group (2800 cm^{-1}), a benzene ring (1610 cm^{-1}), and an unsubstituted cyclopentadienyl group (1105 and 1000 cm^{-1}).

1-*exo-(Trimethylsilyl)-2,3-ferrocenoindene* (*Ia*)

To a dispersion of 1.0 g (0.14 g-atom) of lithium in 100 ml of THF was added over a period of 10 min a solution of 3.0 g (0.0099 mole) of (IIb) in 50 ml of THF at −10 to −5°, yielding a deep-red solution. The solution after stirring for 20 min, was added dropwise to a solution of 2.0 g (0.018 mole) of trimethylchlorosilane in 50 ml of THF with cooling in an ice-bath. The mixture was stirred for 30 min and then hydrolyzed. The resulting organic layer and benzene/hexane (1/1) extracts from the aqueous layer were combined, washed with water, and dried over anhydrous sodium sulfate. After evaporation of the solvents, the residue was chromatographed over alumina using petroleum ether as an eluant and then fractionally distilled to give 2.5 g (72% yield) of 1-*exo*-(trimethylsilyl)-2,3-ferrocenoindene (Ia), b.p. 132–134°/0.029 mmHg, m.p. 68–68.5° (recrystallized from methanol) (Found: C, 69.35; H, 6.05. $C_{20}H_{22}FeSi$ calcd.: C, 69.36; H, 6.40%.). IR: 1610, 1250, 1106 and 1000 cm^{-1}.

1-*endo*-(*Trimethylsilyl*)-2,3-*ferrocenoindene* (*Ib*)

To a solution of 173 mg (0.500 mmole) of (Ia) in 50 ml of THF was added dropwise a solution of 14.5 mmole of n-butyllithium in 10 ml of hexane with cooling in an ice-bath. The reaction mixture turned dark-red and was stirred with cooling for 1 h. It was then hydrolyzed and the resulting organic layer was separated. The aqueous layer was extracted with petroleum ether and the combined organic layer was dried over anhydrous sodium sulfate. After evaporation of the solvents, the residue was chromatographed over alumina using petroleum ether as an eluant to give 146 mg (84.4% yield) of 1-*endo*-(trimethylsilyl)-2,3-ferrocenoindene (Ib), m.p. 68–71° (recrystallized from methanol). (Found: C, 69.47; H, 6.55. $C_{20}H_{22}FeSi$ calcd.: C, 69.36; H, 6.40%.) IR: 1610, 1250, 1107 and 1000 cm^{-1}. Another run involving alcoholysis by tert-butyl alcohol instead of hydrolysis gave the same result.

Methanolysis of (*Ia*) *in the presence of anhydrous ferric chloride*

In a two-limbed glass tube were placed separately a solution of 124 mg (0.348 mmole) of (Ia) in 5 ml of absolute methanol, and a solution of 113 mg (0.696 mmole) of anhydrous ferric chloride in 5 ml of absolute methanol. These solutions were degassed by several freeze-thawings *in vacuo*. The tube was then sealed under vacuum and the two solutions were mixed at room temperature. The mixture immediately turned dark-green, indicating the formation of ferricenium ions, and then rapidly turned brown. After standing for 10 min, the solution was then added to water (50 ml) and the mixture was extracted twice with 30 ml-portions of petroleum ether. The extracts were dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed over alumina using petroleum ether as an eluant to give 87.5 mg (82.7% yield) of oily 1-*exo*-methoxy-2,3-ferrocenoindene (IIa). (Found: C, 71.35; H, 5.59. $C_{18}H_{16}FeO$ calcd.: C, 71.08; H, 5.30%.) IR: 2810, 1611, 1107, and 1000 cm^{-1}. In a second run, (Ia) (113 mg, 0.317 mmole) was similarly allowed to react with $FeCl_3$ (103 mg, 0.636 mmole) in methanol (10 ml) at room temperature for 42 h. After work-up as above, 55.4 mg (57.5% yield) of a mixture of (IIa) and (IIb) in the ratio of 1.7/1 (determined by the NMR spectroscopy) was obtained.

Methanolysis of (*Ib*) *in the presence of anhydrous ferric chloride*

In essentially the same manner 105 mg (0.303 mmole) of (Ib) was allowed to react with 98.3 mg (0.606 mmole) of anhydrous ferric chloride in methanol (10 ml) at room temperature for 10 min. After work-up, 70.0 mg (76.0% yield) of (IIa) was obtained. In a second run, (Ib) (40.0 mg, 0.116 mmole) was similarly treated with $FeCl_3$

(38.6 mg, 0.232 mmole) in methanol (10 ml) at room temperature for 1 h. After work-up 27.6 mg (78.2% yield) of a mixture of (IIa) and (IIb) in the ratio of 4.9/1 was obtained.

Acid-catalyzed epimerization of (IIa) and (IIb)

In a two-limbed glass tube were placed separately a solution of 29.7 mg (0.0976 mmole) of (IIa) in 9 ml of absolute methanol and 1 ml of a 2.24 *M* methanolic solution of hydrogen chloride. These solutions were degassed by several freeze-thawings under vacuum. The tube was evacuated, then sealed, and the two solutions were mixed at room temperature. The mixture was allowed to stand at room temperature for 46 h. After work-up, chromatography over alumina using ether as an eluant gave 26.1 mg (87.9% yield) of a mixture of (IIa) and (IIb) in the ratio of 2.0/1.

Similarly, (IIb) (47.2 mg, 0.155 mmole) was allowed to react in a 0.224 *M* methanolic solution (10 ml) of hydrogen chloride at room temperature for 40 h. Chromatography gave 37.5 mg (79.4% yield) of a mixture of (IIa) and (IIb) in the ratio of 4.0/1.

REFERENCES

1 T. Kondo, K. Yamamoto and M. Kumada, *J. Organometal. Chem.*, 35 (1972) C30.
2 M. Cais, A. Modiano and A. Raveh, *J. Amer. Chem. Soc.*, 87 (1965) 5607.
3 D. E. Bublitz, W. E. McEwen and J. Kleinberg, *J. Amer. Chem. Soc.*, 84 (1962) 1845.
4 M. Le Plouzennec and R. Dabard, *C. R. Acad. Sci.. Ser. C*, 268 (1969) 1721.
5 A. N. Nesmeyanov, E. G. Perevalova and Yu. A. Ustynyuk, *Dokl. Akad. Nauk SSSR*, 133 (1960) 1105.
6 T. D. Turbitt and W. E. Watts, *Tetrahedron*, 28 (1972) 1227.
7 T. J. Katz and M. Rosenberger, *J. Amer. Chem. Soc.*, 85 (1963) 2030.
8 G. Marr and J. Ronayne, *J. Chem. Soc. D*, (1970) 350.
9 D. S. Trifan and R. Bacskai, *Tetrahedron Lett.*, (1960) 1.
10 E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, 83 (1961) 840, 4216.
11 M. Rosenblum and F. W. Abbate, *J. Amer. Chem. Soc.*, 88 (1966) 4178.
12 M. J. Nugent and J. H. Richards, *J. Amer. Chem. Soc.*, 91 (1969) 6138.