Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REACTIONS OF FERROCENYLCARBENE IV*. THE SYNTHESIS OF [3]-FERROCENOPHAN-2-ONE TOSYLHYDRAZONE AND THE THERMAL DECOMPOSITION OF ITS SODIUM SALT

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(Received June 11th, 1970; by publisher August 31st, 1970)

SUMMARY

A practical synthesis of 1,1'-ferrocenediacetic acid (Va), the starting material for the preparation of [3]-ferrocenophan-2-one (VI) has been accomplished by successive reactions starting from 1,1'-ferrocenedicarboxylic acid (IIIa). The synthesis of the tosylhydrazone (VII) and thermal decomposition of its sodium salt have been described. Ferrocenophane-β-carbene generated in the thermal decomposition has been suggested to be triplet.

INTRODUCTION

In the previous works[1] on the thermal decomposition of acylferrocene tosylhydrazone sodium salt, it has been found that α-ferrocenylcarbenes (I, $R = H$, CH_3, and C_6H_5) are all triplet; these carbenes react as radical species affording hydrogen or halogen abstraction products from solvents and react easily with oxygen [2] and they add to particular olefins such as 1,1-diphenylethylene[3]. Further, we have pointed out that the triplet nature of these carbenes may be attributed to an adjacent ferrocenyl group.

It is widely known[4] that arylcarbenes are triplet and the triplet nature is due to the presence of adjacent aromatic moiety[5]. On the other hand, the effect of aromatic nucleus on the spin state of a carbene is known[6] to be insulated by a methylene group by the investigation of chemical reactions of benzylcarbene.

On this basis, in order to elucidate the direct interaction of Fe metal in the reaction of ferrocenylcarbene, the investigation of the reaction of a β-ferrocenylcarbene (II), in which a divalent carbon is separated from two aromatic cyclopentadienyl rings by two methylene groups at both sides and is located directly before Fe atom, was attempted. In this paper, we wish to report the synthesis of the corresponding tosylhydrazone and some reactions of the carbene generated by the thermal decomposition[7] of the sodium salt of the tosylhydrazone.

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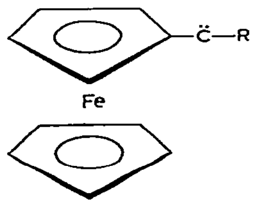
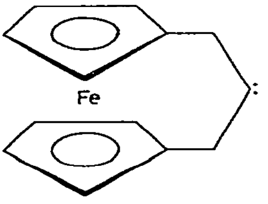
* Presented at the 22nd annual meeting of Japan Chemical Society, Tokyo, April 2, 1969. Part III see *Bull. Chem. Soc. Japan*, 43 (1970) in press.



(I)(R=H, CH_3, C_6H_5)



(II)

RESULTS AND DISCUSSION

The preparation of [3]-ferrocenophan-2-one tosylhydrazone (VII)

In connection with our current interest in the reaction of β-ferrocenylcarbene (II), it became desirable to synthesize [3]-ferrocenophan-2-one (VI) in quantity. Although the synthesis of (VI) starting from dimethyl-1,1′-ferrocenediacetate (Vb) is established by Mock and Richards[8], it was found that the preparation of the starting diester (Vb) in practical quantity by the reported procedure[9] is not satisfactory. Thus, according to the reported procedure, Willgerodt–Kindler reaction of 1,1′-diacetylferrocene was examined repeatedly, but this procedure resulted in the formation of diacetic acid (Va) in a poor yield by our hands (< 1 %) and afforded a large amount of tarry material. Further, all attempts to improve the low yield of (Va) by modification of reaction conditions were failed. Therefore, it was necessary to develop another route for the preparation of (Va) in quantity.

As preliminary experiments, two procedures: Arndt–Eistert reaction of 1,1′-ferrocenedicarboxylic acid dichloride*, and Clemmensen reduction of 1,1′-ferrocenediglyoxalic acid** which was derived from the selenium dioxide oxidation of 1,1′-diacetylferrocene followed by oxidation with Ag_2O, were tried but these reactions did not afford any amount of (Va).

After the unsuccessful attempts to prepare (V) by above mentioned procedures, it has been found finally that (V) can be prepared in a good yield in sizable scale by successive reactions of lengthening carbon chains as shown in Scheme 1.

In this connection, it became necessary to prepare 1,1′-ferrocenedicarboxylic acid (IIIa) in large quantity. Although the synthetic methods of (IIIa) have been reported by many workers[12], the large scale preparation of the acid is not so easy. But, when 1,1′-diacetylferrocene was treated with sodium hypobromide in dioxane/water below 5° (the reaction temperature is essential; at a temperature higher than 5°, rapid decomposition of ferrocene nuclei takes place), it has been found that (IIIa) is obtained at a yield of 85–90 % and this reaction can be adopted in large scale preparation of (IIIa).

Then, 1,1′-bis(hydroxymethyl)ferrocene (IVa) was synthesized in a 75 % yield by usual $LiAlH_4$ reduction of the dimethylester (IIIb) which was prepared by acid catalysed esterification of (IIIa).

It was found that when the reaction of (IVa) with PCl_3*** was carried out in THF under nitrogen atmosphere, the dichloride (IVb) was obtained in a high yield

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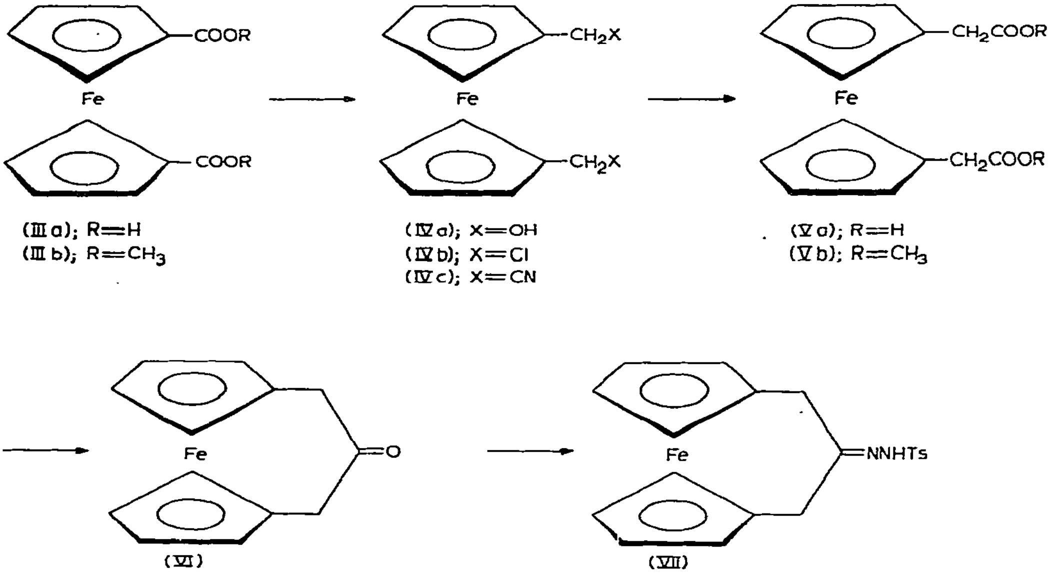
* Prepared by the procedure reported by Goldberg[10].

** On the other hand, this method afforded ferroceneacetic acid in a low yield from acetylferrocene. The acid was confirmed by IR and m.p. (159–160°, lit.[11] 161°).

*** PCl_3 is known to be a good reagent for chlorination of hydroxymethylferrocene[13].

SCHEME 1



(IIIa); R=H
(IIIb); R=CH₃

(IVa); X=OH
(IVb); X=Cl
(IVc); X=CN

(Va); R=H
(Vb); R=CH₃

(VI)

(VII)

(87%). Then (IVb) was converted into dinitrile (IVc) in a 95% yield by the reaction in THF with aqueous KCN. The compound (IVc) was hydrolysed in boiling alcoholic sodium hydroxide to (Va) (72% yield) which was esterificated with diazomethane in ether.

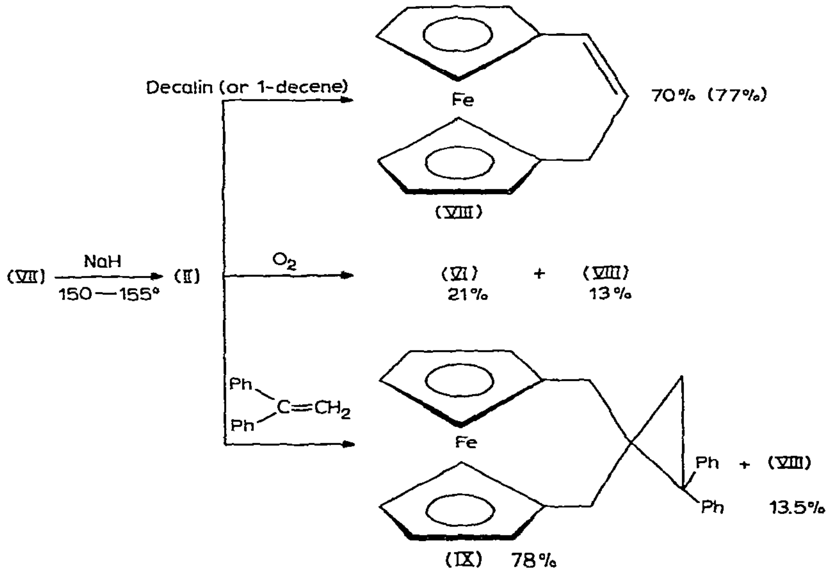
Thus, a preparative method of (Va) has been established, then (Vb) obtained was converted into (VI) according to Mock–Richards procedure in a 88% yield, and the tosylhydrazone (VII) was prepared from (VI) by the reaction with a slight excess of *p*-toluenesulfonylhydrazine in boiling methanol in a 86% yield.

Thermal decomposition of sodium salt of (VII)

The thermal decomposition of [3]-ferrocenophan-2-one tosylhydrazone sodium salt, prepared by reaction of (VII) with sodium hydride, was carried out in a mixture of dry pyridine and decalin under inert gas atmosphere. It was observed that the decomposition took place at 150–155° with rapid evolution of nitrogen gas. This reaction gave 1,2-dehydro-[3]-ferrocenophane[14] (VIII) in a 70% yield besides an unidentified polymeric material.

When the decomposition reaction was performed in the presence of oxygen, [3]-ferrocenophan-2-one (VI) and (VIII) were obtained in 21% and 13% yield respectively. It is noteworthy that (VI) is afforded in this reaction, suggesting that carbene (II) generated in the decomposition reaction of the salt of (VII) reacts as a triplet, since it is well known that oxygen is an effective triplet carbene acceptor[2].

Next, addition reactions of the carbene to olefin were examined. When the decomposition was performed in the presence of large excess of 1,1-diphenylethylene, the addition product (IX) was obtained in a high yield (78%) besides a small amount of olefin (VIII) (13%). The structure of this interesting ferrocenyl spirane derivative was confirmed by NMR, IR, molecular weight measurement and elemental analysis. Since 1,1-diphenylethylene is known to be an effective triplet carbene trapping reagent[3], the formation of spirane (IX) might be explained by the addition of triplet carbene (II) to the olefin. On the other hand, in the decomposition in 1-decene under similar conditions, (VIII) was obtained as one and only isolated product in 77% yield. In addition, the decomposition reaction in an equimolar mixture of 1,1-diphenylethylene and 1-decene gave (IX) and (VIII) in 45% and 29% yields respectively. In these decomposition reactions, the formation of addition product to 1-decene could not be observed. These results obviously indicate that there is a large difference on the reactivity between 1,1-diphenylethylene and 1-decene in the reaction of carbene (II); hence it may be deduced that the reacting carbene is triplet[3].



Of course, the hydrogen transfer reaction forming olefin (VIII) proceeds most probably via singlet stage of the carbene[15]. Therefore, it is reasonable to consider that singlet–triplet competitive reaction of the carbene is involved in the reaction.

It is the first example that a carbene whose substituents are aralkyls reacts as a triplet species. This result suggests that there must exist an effect of Fe metal on the spin state in this particular β-ferrocenylcarbene.

Now, the stereochemical investigation on the addition reaction course of the carbene is underway.

EXPERIMENTAL

IR spectra were recorded on a Hitachi EPI-S2 spectrophotometer and NMR spectra on a JEOLCO JNM-MH-60 (Minimar 60) at 60 MHz or a JEOLCO JNM-4H-100 at 100 MHz using TMS as an internal standard. All temperatures were uncorrected.

Dimethyl 1,1′-ferrocenedicarboxylate (IIIb)

To a solution of 1200 ml of water containing 200 g of NaOH was dropwise added 230 g of bromine at 0–10° with mechanical stirring. Then 600 ml of dioxane was added in portions. At a temperature of 0–5° (ice/salt bath was required), 62.0 g of finely powdered 1,1-diacetylferrocene[16] was added in small portions (about 1 g) to the vigorously stirred solution. After addition was over (80 min), stirring was continued for one hour at those temperatures. The reaction mixture was filtered and the filtrate was washed with CH_2Cl_2 three times and then aqueous layer was heated up to 80°. Then the hot solution was acidified with conc. HCl. Fine deep red crystals deposited which were collected and washed with water and dried. There obtained 57.0 g of (IIIa), m.p. >250°, 91%. The IR spectrum was identical with that of authentic acid[12b].

The mixture of 44.0 g of crude (IIIa) and 600 ml of methanol containing 3 ml of conc. H_2SO_4 was heated under reflux for 25 h, then cooled to room temperature. (IIIb) deposited as brown crystals, m.p. 112–114°, 44.0 g (90%), which was recrystallized from methanol, m.p. 113–114° (lit.[17] 114–115°). IR (Nujol): 1700 s (C=O), 1375 s, 1285 s, 1195 m, and 1145 s, cm^{-1}.

1,1'-Bis(hydroxymethyl)ferrocene (IVa)

The reported procedure[18] for preparation of (IVa) was modified. To a mixture of 7.0 g of $LiAlH_4$ and 800 ml of dry ether, was added dropwise a solution of 28.7 g (0.095 mole) of (IIIb) dissolved in 400 ml of dry benzene at room temperature with mechanical stirring. After the solution was heated under reflux for 3 h, the reaction mixture was decomposed with a small amount of cold water. In this reaction, 23.0 g of (IVa) was obtained, m.p. 107–108° (lit.[18,19] 108.5–109.5°, 107–108°), 98% yield.

1,1'-Bis(chloromethyl)ferrocene (IVb)

A solution of 1.5 g of freshly distilled PCl_3 and 15 ml of dry THF was added dropwise to a solution of 3.0 g (1.22 mmole) of (IVa), 0.6 ml of dry pyridine and 75 ml of dry THF with stirring under nitrogen atmosphere (slightly exothermic). After addition was over, stirring was continued for 3 h at room temperature. Then the solution was decanted and the residue was rinsed with 30 ml of THF. The combined solution was evaporated under reduced pressure. (IVb) was obtained as residual yellow crystals, m.p. 95–98°, recrystallization from hexane, m.p. 97–98°, 3.0 g (87%). (Found: C, 51.24; H, 4.36; Cl, 24.43. $C_{12}H_{12}Cl_2Fe$ calcd.: C, 50.93; H, 4.27; Cl, 24.06%.) IR (Nujol): 1400 w, 1378 m, 1363 s, 1263 s, 1050 w, 1038 m, 1025 m, 926 w, 905 w, 840 s, 820 w, 725 s, and 660 s, cm^{-1}.

1,1'-Bis(cyanomethyl)ferrocene (IVc)

In the preparative work, (IVc) was synthesized from (IVa) without isolating dichloride (IVb). To a solution of 10.0 g (0.038 mole) of (IVa) and 200 ml of dry THF containing 2 ml of pyridine was added a solution of 5.0 g of PCl_3 and 20 ml of THF and reacted for 3 h as described above. The resulting solution was transferred to a dropping funnel under nitrogen stream. In a 1000 ml three necked flask, 30 g of KCN was dissolved in 60 ml water, then the flask was flushed with nitrogen. To the solution was added the above THF solution dropwise with rapid stirring at room temperature and occasional cooling with ice bath (exothermic). After the addition was completed, the mixture was stirred another hour. The THF layer which was separated from the aqueous phase, was washed with saturated salt water 3 times and dried over anhydrous sodium sulfate. Crude (IVc) was obtained as brown crystals when the solution was evaporated under reduced pressure, 9.5 g, m.p. 70–73°, 89% yield. Recrystallization from hexane gave yellow crystals, m.p. 73–74°. (Found: C, 63,61; H, 4.74; N, 10.50. $C_{14}H_{12}FeN_2$ calcd.: C, 63.67; H, 4.62; N, 10.61%.) IR (Nujol): 3140 w, 2260 m, 1408 m, 1300 m, 1237 m, 1210 w, 1193 w, 1061 w, 1041 s, 1029 s, 938 m, 925 m, 910 s, 851 s, and 825 s cm^{-1}. NMR (60 MHz) $\delta(CCl_4)$: 4.43 ppm (s, 8 H, ferrocenyl) and 3.57 ppm (s, 4 H, methylene).

1,1'-*Ferrocenediacetic acid* (*Va*)

A mixture of 9.5 g (0.036 mole) of (IVc), 50 ml of ethanol, 80 ml of water and 10.0 g of NaOH was boiled under reflux. After the slow evolution of NH_3 ceased (4–5 h), the mixture was cooled to room temperature and was washed twice with ether. The acidification of resulting dark red alkaline solution with 60 ml of 6 *N* HCl afforded fine brown crystals contaminated with a small amount of black tarry material. The crude acid was dissolved in 100 ml of saturated sodium bicarbonate solution. Then the solution was washed with ether. When the bicarbonate solution was acidified with 6 *N* HCl, fine yellow plates deposited which were collected, washed with cold water and dried. There obtained (Va), 8.1 g, m.p. 165° sintered 175–178° decompn., (lit.[9] 140–143° decompn.), 72% yield. IR (Nujol): 1713 s (C=O), 1693 w, 1418 w, 1405 w, 1329 m, 1295 m, 1240 s, 1212 s, 1161 m, 1041 m, 1023 m, 945 m, 930 m, 825 m, 775 m, and 664 m cm^{-1}. Since (Va) was found to be considerable unstable in hot THF, methanol and $CHCl_3$, it was converted to dimethylester (Vb) without further purification. On esterification with diazomethane, 8.0 g of (Va) afforded 8.5 g of heavy reddish brown oil which was purified by distillation giving 8.0 g of (Vb) (94%), b.p. 140–145° (0.01 mm). (Found: C, 58.65; H, 5.63. $C_{16}H_{18}FeO_4$ calcd.: C, 58.21; H, 5.50%.) IR (liquid film): 3130 w, 2980 m, 1740 s, 1460 w, 1435 m, 1315 m, 1265 s, 1231 s, 1200 w, 1145 s, 1041 m, 1012 m, 923 w, 830 m, and 812 w cm^{-1}. NMR (100 MHz) $\delta(CCl_4)$: 4.04 and 3.98 ppm (two peaks, 8 H, ferrocenyl), 3.67 ppm (s, 6 H, methyl) and 3.98 ppm (s, 4 H, methylene).

[3]-*Ferrocenophan-2-one* (*VI*)

According to Mock and Richards procedure, (VI) (4,4 g) was synthesized starting from 7.0 g (0.021 mole) of (Vb) (86%). Yellow plates, m.p. 155–156°, (lit.[8] m.p. 154–155°). IR (Nujol): 1690 s (C=O), 1433 w, 1377 w, 1366 w, 1268 m, 1210 w, 1160 w, 1068 w, 1036 w, 1025 s, 933 m, 875 w, 866 w, 850 w, and 810 s cm^{-1}. NMR (60 MHz) $\delta(CCl_4)$: 4.33 and 4.20 ppm (two multiplet peaks, 8 H, ferrocenyl) and 3.10 ppm (s, 4 H, methylene).

[3]-*Ferrocenophan-2-one tosylhydrazone* (*VII*)

A mixture of (VI), 3.0 g (0.0125 mole), tosylhydrazine[20], 2.5 g (0.0134 mole) and 135 ml of methanol was boiled for 3 h. The compound (VII) deposited even in boiling as bright brown crystals, 4.4 g, m.p. 220–223° decompn., 86% yield. (Found: C, 58.74; H, 4.90; N, 6.96. $C_{20}H_{20}FeN_2O_2S$ calcd.: C, 58.83; H, 4.94; N, 6.86%.) IR (Nujol): 3230 s (N–H), 1600 m, 1425 w, 1382 m, 1331 s, 1310 w, 1292 w, 1227 w, 1164 s, 1096 m, 1028 s, 855 m, 840 w, 812 s, 806 w, 769 m, 708 m, 695 w, and 679 m cm^{-1}. NMR (60 MHz) $\delta(CDCl_3)$: 8.0–7.3 ppm (complex peaks, 4 H, phenyl), 7.21 ppm (s, 1 H, N–H), 5.04 and 4.94 ppm (two multiplet peaks, 8 H, ferrocenyl), 2.95 ppm (s, 4 H, methylene) and 2.73 ppm (s, 3 H, methyl).

Thermal decompositions of sodium salt of (VII)

Reaction in decalin under nitrogen atmosphere. To a solution of (VII) (0.244 g, 0.6 mmole) in dry pyridine (0.8 ml) was added NaH (1 mmole). After rapid evolution of hydrogen ceased, dry decalin (3 ml) was added to the mixture. Then the atmosphere was replaced with nitrogen. When the mixture was heated in an oil bath, rapid decomposition took place with evolution of nitrogen gas at 150–155°. After gas evolution was completed, the reaction mixture was cooled and poured onto cracked ice, then extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate and evaporated to give residual decalin solution. After decalin was distilled off under reduced pressure (80°/100 mm), remaining brown substance was subjected to an elution chromatography using 5 g of Florisil (100–200 mesh). Hexane eluted 0.094 g of (VIII), m.p. 100.5–103°, 70 % yield, which was purified by sublimation, m.p. 101–103° (lit.[14] m.p. 100.5–102.5°). (Found: C, 69.62; H, 5.61. $C_{13}H_{12}Fe$ calcd.: C, 69.68; H, 5.40%.) IR (Nujol): 1641 w (C=C), 1200 m, 1042 m, 1035 m, 1020 s, 890 m, 860 m, 848 m, 808 s, and 723 s cm^{-1}. NMR (60 MHz) $\delta(CS_2)$: 6.03 ppm (s, 2 H, vinyl), 3.93 ppm (m, 8 H, ferrocenyl) and 2.82 ppm (s, 2 H, methylene).

Reaction in the presence of oxygen. A mixture of (VII) (0.236 g, 0.58 mmole) NaH (1 mmole), pyridine (3 ml) and decalin (3 g) was heated at 150–155° under O_2 atm. Resulting mixture was treated as above, the product mixture was chromatographed on a column of 10 g of Florisil. Pentane eluted (VIII), 0.014 g, m.p. 96–99°, 13 %, which was identified by mixed m.p. and IR spectrum. Benzene eluted 0.032 g of (VI), m.p. 152–154°, which was identified by the comparison of IR spectra and mixed m.p. with authentic sample (21 % yield). Elution with ether/methanol afforded an unidentified black tarry material.

Reaction in the presence of 1,1-*diphenylethylene.* A thermal decomposition was performed using 0.210 g (0.514 mmole) of (VII) in the presence of 1,1-diphenylethylene[21] (6 g) instead of decalin. Resulting mixture was extracted with 100 ml of hexane. The extract was washed with water, dried over anhydrous sodium sulfate and the solvent was evaporated. Residual yellow oil was distilled under reduced pressure (110°/4 mm). The distillate (5.6 g), unreacted diphenylethylene, was contaminated by a yellow substance, which was separated by an alumina elution chromatography (150 g of alumina) and identified to be (VIII) (0.017 g, 13.5 %) by mixed m.p. and IR. The bottom substance which deposited as yellow crystals was chromatographed on alumina (20 g) with hexane elution, giving 0.162 g of (IX), m.p. 239–240°, 78 % yield. (Found: C, 80.39; H, 5.99; mol. wt. 378 (VPO, benzene). $C_{27}H_{24}Fe$ calcd.: C, 80.20; H, 5.98 %; mol. wt., 404.35) IR (Nujol): 1597 w, 1495 m, 1290 w, 1250 w, 1224 w, 1207 w, 1130 w, 1068 m, 1040 s, 1025 m, 1017 w, 1000 w, 940 m, 910 m, 868 w, 849 s, 822 w, 810 s, 803 s, 768 m, 742 m, 706 s, and 693 m cm^{-1}. NMR (60 MHz) $\delta(CS_2)$: 7.7–7.3 ppm (complex peaks, 10 H, phenyl), 4.10 ppm (m, 8 H, ferrocenyl), 2.21 and 1.58 ppm (AB quartet, J(AB) 15.0 Hz, 2+2 H, methylene) and 1.57 ppm (s, 2 H, methylene protons of cyclopropane).

Reaction in the presence of 1-*decene.* A thermal decomposition was carried out in a sealed tube containing a mixture of the sodium salt [(VII), 0.157 g, 0.385 mmole], pyridine (0.6 ml) and freshly distilled 1-decene (4 g) at 160°. Resulting mixture was treated as usual. After decene was distilled off under reduced pressure (65–70°/45 mm), dark residue was subjected to an alumina chromatography (10 g of alumina). Hexane eluted (VIII) (0.067 g, m.p. 101–102.5°, 77% yield) which was identified by IR and mixed m.p. Elution with ether/methanol gave a tarry black mass (0.04 g).

Reaction in the mixture of 1,1-*diphenylethylene and* 1-*decene*. The salt of (VII) (0.156 g, 0.383 mmole) in 4 g of equimolar mixture of two olefins was decomposed in the similar manner as above. From diphenylethylene distillate, (VIII) was isolated by alumina chromatography (0.024 g, 29% yield). The bottom substance was chromatographed on alumina giving adduct (IX) (0.068 g, 45% yield), m.p. 238–240°, identified by IR and mixed m.p.

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