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REACTIONS OF FERROCENYL CARBENE. I. THERMAL DECOMPOSITION OF ACYLFERROCENE TOSYLHYDRAZONE SODIUM SALT

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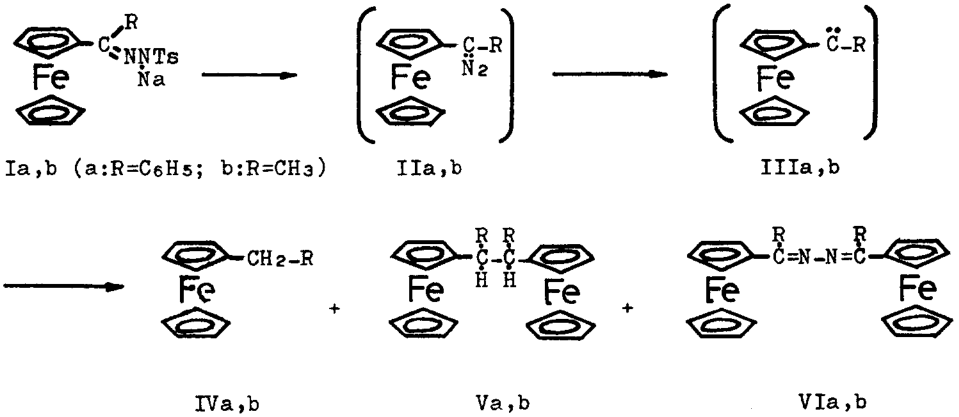
On account of an interest to study the effect of a transition metal on the spin state of a carbene, we have investigated the reactions of some α-ferrocenyl carbenes in these years. A recent report by M. Cais et al.(1) on a possible formation of ferrocenyl carbene in the deprotonation of ferrocenyl carbonium ion prompted us to report our results on the chemistry of ferrocenyl carbenes.

The thermal decomposition of benzoylferrocene tosylhydrazone sodium salt (Ia), prepared in situ by a reaction of corresponding hydrazone (mp 166.5°(decomp)) with sodium hydride, was carried out in pyridine-cyclohexene at 80°. Although the isolation of diazo compound IIa was unsuccessful, its intermittent formation was indicated by IR (2060cm^{-1}).(2) There were isolated benzylferrocene* (IVa, mp 75-76°, 27%),(3) diastereomers of 1,2-diferrocenyl-1,2-diphenylethane* (Va, mp 217-220°,



Ia,b (a:R=C$_6$H$_5$; b:R=CH$_3$) IIa,b IIIa,b

IVa,b Va,b VIa,b

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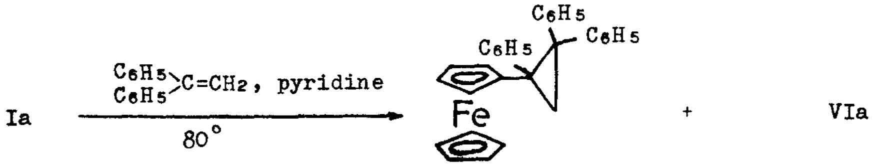
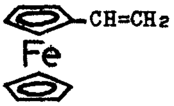
* The material with an asterisk was confirmed by a comparison with authentic specimen. The compounds without it were characterized by elemental analysis, IR, UV, and nmr spectroscopy. The melting points are uncorrected.

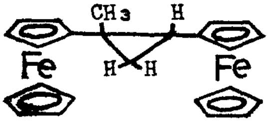
and Va', mp 277-280°, 1.5%),(4) and benzoylferrocene azine (VIa, mp 157°, 36%), but no addition product of the carbene to cyclohexene was detected. Also the decomposition in pyridine-ethyl vinyl ether gave no addition product but the compounds obtained were IVa (44%) and VIa (trace). On the other hand, the decomposition in 1,1-diphenylethylene-pyridine yielded the addition product VII (mp 175-176°, 14%) besides VIa (33%). It is reasonable to consider that all of these products are derived from ferrocenylphenyl carbene (IIIa).



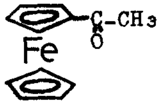
The reaction products obtained in the reaction of ferrocenylmethyl carbene (IIIb) were somewhat complex. The three products as above, i.e. ethylferrocene* (IVb, bp 106-114°/8mm, 2.1%);(5) 2,3-diferrocenyl-n-butane (Vb, streoisomeric mixture, 0.6%), and the azine (VIb, mp 211-212°, 2.5%), were also obtained in appreciable yields, but compounds produced in larger amounts were vinylferrocene*(VIII, mp 49-52°, 41%),(6) 1,2-diferrocenyl-1-methylcyclopropane (IX, mp 155°, 0.4%);** acetylferrocene*(X, mp 84-86°, 8.8%),(7) and ferrocenylmethylcarbinol*(XI, mp 73-76°, 3.4%).(8)



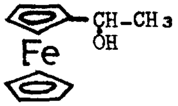
VIII



IX



X



XI

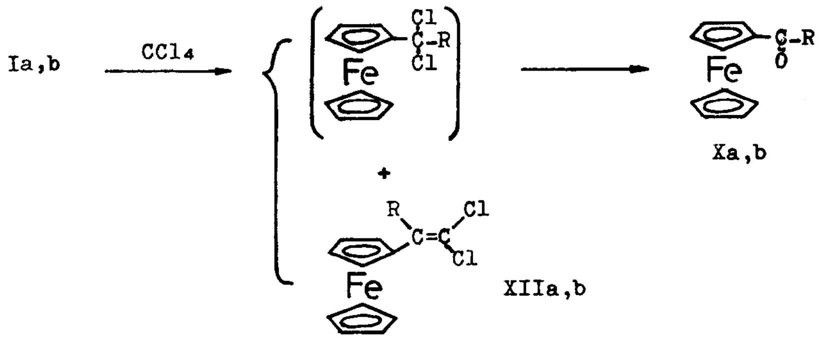
A very similar mixture was also obtained in the decomposition of IIb prepared by the oxidation of acetylferrocene hydrazone (mp 110-111.5°) with yellow mercuric oxide. When the decomposition was carried out in cyclohexene, there were obtained IVb (trace), Vb (2.3%), VIb (12%), VIII (16%), IX (2%), X (9%), and XI (2%); no addition product was detected again. It is notable to point out that the product mixture yielded in the decomposition in benzene lacks IVb and Vb.

** Unfortunately, the data did not allow to elucidate the stereochemistry of IX.

Now, the formations of IV and V in the presence of cyclohexene or ethyl vinyl ether strongly indicate that the carbene involved is a triplet. It is rationalized in a way that the carbene abstracts a hydrogen from the solvent to give an intermediate radical, which abstracts the second hydrogen to afford IV or couples to give V. The fact that the carbene adds easily to 1,1-diphenylethylene also suggests the triplet nature, since this particular olefin has been known to be an effective triplet carbene trapper.(9)

The formation of 1,2-diferrocenyl-1-methylcyclopropane (IX) is rationalized by the addition of ferrocenylmethyl carbene (IIIb) to vinylferrocene (VIII). It is to be noted that IIIb adds apecifically to the double bond of VIII in spite of the co-existence of a large excess of cyclohexene. This also indicates that the carbene is a triplet, because the competitive studies(10) have shown that a triplet carbene such as diphenyl carbene adds selectively towards styrene or vinylferrocene while a singlet carbene such as dichlorocarbene adds equally well to cyclohexene, styrene, and vinylferrocene. After these discussions, it becomes clear that the ferrocenyl carbenes have reacted in their triplet state.

There are still other evidences indicating the triplet nature. When Ia was decomposed in the presence of oxygen, the major product was benzoylferrocene, which was hardly found in the decomposition under a nitrogen stream.(11) Moreover, the decomposition of Ia in carbon tetrachloride resulted in the formations of chlorine abstracted products, benzoylferrocene* (Xa, mp 108-109°, 12%)(12) and 2-ferrocenyl-2-phenyldichloroethylene (XIIa, mp 128.5-129°, 17%). The decomposition of Ib also yielded acetylferrocene (Xb, 9%) and 2-ferrocenyl-2-methyldichloroethylene (XIIb, mp 52-53°, 3%). The acylferrocenes are considered to be produced by the hydrolysis of dichloroferrocenylmethyl derivatives,(13,14) and the dichloroethylenes are derived from the coupling between the carbene and trichloromethyl radical followed by a loss of a chlorine atom.(14)



In conclusion, it can be said that the ferrocenyl carbene preferably undergoes radical reactions and hence it is a triplet. The triplet nature might be attributed to an adjacent ferrocenyl group. This triplet ferrocenylcarbene reacts preferentially with vinylferrocene even though a large excess of cyclohexene co-exists in the reacting mixture.

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