

FUNDAMENTAL STUDIES OF SUBSTITUTED FERROCENE  
SYSTEMS. II. RACEMIZATION OF (+)-1,2-( $\alpha$ -KETOTETRAMETHYLENE)FERROCENE.<sup>1</sup>

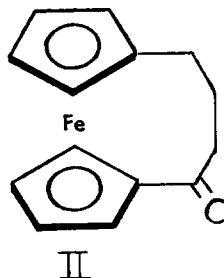
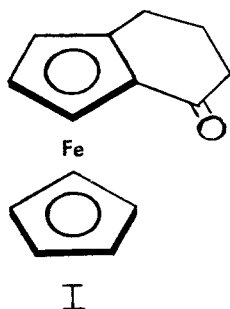
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Studies of the racemization of many classes of molecules have led to information concerning processes that take place within the molecule. Several examples of optically active metallocenes are known.<sup>2</sup> No reports have yet appeared of the racemization of any such compound. We now wish to report the racemization of optically active 1,2-( $\alpha$ -ketotetramethylene)-ferrocene (I), coincidentally the first metallocene to be resolved.<sup>3</sup> In addition we wish to suggest that this racemization takes place via a novel ligand exchange or ligand inversion mechanism.

Optically active ketone I was racemized in refluxing nitromethane with aluminum chloride. Each run was monitored by tlc, gc, nmr, ir and elemental analysis to insure that the decrease in specific rotation could not be significantly attributed to decomposition or the presence of impurities. A typical run involved 0.6861g of ketone I, mp 78-79° of  $[\alpha]_{\text{Hg}}^{25^\circ} + 292^\circ$ .<sup>4</sup>



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Anal. Calcd. for  $C_{14}H_{14}FeO$ : C, 66.17; H, 5.55; Fe, 21.98.

Found: C, 66.09; H, 5.72<sup>5</sup>; one peak on 3% SE 30 on Chromosorb P column, retention time 7.20 min. This material was added to 0.520g aluminum chloride (freshly opened) in 60ml freshly distilled nitromethane and refluxed for 60 min. The reaction mixture was hydrolyzed with 100 ml water, the ketone extracted with ether, concentrated, and rapidly chromatographed on alumina III using diethyl ether as eluent. The red solid obtained was sublimed<sup>6</sup> to give 0.5754g recovered ketone (83.5%): mp. 78-79°,  $[\alpha]_{Hg}^{25^\circ} + 160^\circ$ , Anal. Found: C, 66.15; H, 5.36; Fe, 21.78.<sup>5</sup> Samples of ketone taken before and after the racemization possessed superimposable ir and nmr spectra as well as identical tlc and gc chromatograms.

That aluminum chloride was required in the racemization process was demonstrated by the following blank experiment. A sample of ketone I ( $[\alpha]_{Hg}^{25^\circ} + 525^\circ$ ) was refluxed in nitromethane without aluminum chloride for 60 min. Using the procedure described above ketone I was 80% recovered and had a specific rotation of  $+515^\circ$ , well within experimental error.

Insufficient data are available at the present time to conclusively demonstrate the mechanisms of this racemization, but, of the three distinct mechanistic possibilities, one is favored. The three possibilities constitute reversible reactions involving ring-acyl bond cleavage, ring-alkyl bond cleavage and substituted ring-iron atom bond fission. Ring acyl bond cleavage is perhaps the least likely since only under extreme conditions does an aromatic carbon-acyl carbon bond break. The nonreversibility of Friedel-Crafts acylation in a related ferrocene system has been demonstrated.<sup>7</sup>

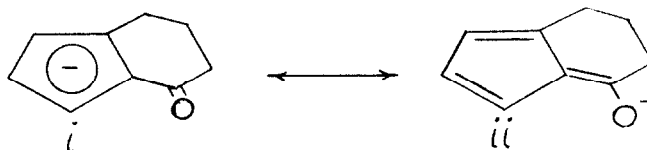
Aromatic ring-alkyl bond cleavage may appear a more likely mechanism since alkyl substituted benzenes are known to undergo rearrangement and/or disproportionation. However, the remaining acyl group should deactivate the substituted ring thereby increasing the possibility of the formation of the heteroannular ring product (II), none of which was found. Even though ketone II was not observed, this mechanistic possibility cannot be ruled out.

Published reports of ligand exchange reactions<sup>8</sup> and disproportionation reactions<sup>9</sup> in the ferrocene system suggest that substituted ring-metal bond

cleavage is the most likely mechanistic process. Aluminum chloride very likely complexes with the substituted ring portion of the ferrocene system resulting in ionization to  $[\text{C}_9\text{H}_9\text{OAlCl}_3^-]^{10}$  and  $[\text{C}_5\text{H}_5\text{Fe}]^+$ . These ions may recombine intramolecularly with inversion or intermolecularly with resulting inversion to lead to the observations reported here. Amplification of our knowledge of this process is being sought through studies on other model systems now in preparation.

## REFERENCES

1. Part I, in preparation. Presented at the Fourth International Conference on Organometallic Chemistry, University of Bristol, July 27-August 1, 1969.
2. For a comprehensive recent review, cf. K. Schlogl in "Topics in Stereochemistry," Vol. I, N. L. Allinger and E. L. Eliel, eds., John Wiley and Sons, New York, N. Y. (1967).
3. J. B. Thomson, Tetrahedron Letters, 26 (1959).
4. The optical measurements were taken at the 546 m $\mu$  Hg line with a Bendix Automatic Polarimeter Series 1100 which was calibrated with both a magnetic standard and a standard sucrose solution before each day's measurements.
5. Elemental analyses by Galbraith Laboratories, Inc., Knoxville, Tenn.
6. Sublimation was determined to be the best method of recovery of pure ketone from the racemization. That  $[\alpha]_{\text{Hg}}^{\text{T}}$  was unaffected by sublimation was shown by several blank experiments in which ketone of known rotations was sublimed. Each time the ketone recovery was >90% and the rotation within experimental error of the starting material.
7. M. Rosenblum, J. O. Santer, and W. Howells, J. Am. Chem. Soc., 85, 1450 (1963).
8. (a) A. N. Nesmeyanov, N. A. Vol'kenau and I. N. Bolesova, Dokl. Akad. Nauk. SSSR, 149, 615 (1963).  
(b) A. N. Nesmeyanov, N. A. Vol'kenau and I. N. Bolesova, Tetrahedron Letters, 1725 (1963).
9. (a) D. E. Bublitz, Can. J. Chem., 42, 2381 (1964).  
(b) D. E. Bublitz, J. Organomet. Chem., 16, 149 (1969).
10. The fragment  $[\text{C}_9\text{H}_9\text{O}]^-$  offers the interesting possibility of being stabilized through resonance structures i and ii. Aluminum chloride then may be complexed by fluctuating



between the sites of negative charge in a manner perhaps not unrelated to the fluxional behavior of certain transition metal  $\pi$ -complexes.