

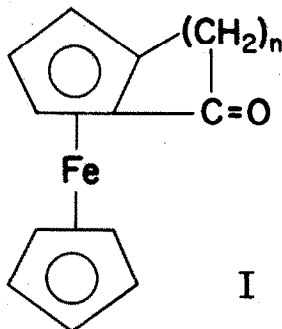
MOLECULAR ASYMMETRY IN THE FERROCENE SERIES

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HOMOANNULAR disubstituted ferrocene derivatives in which the substituents differ are non-superposable on their mirror images and are therefore potentially resolvable. Representatives of this simplest type of asymmetric molecule in the ferrocene series have only recently become available² but



the closely related cyclized compounds (I) have been known for several years³. Optical activity in this latter type of compound has now been

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² D. Lednicer and C. R. Hauser, J. Org. Chem. **24**, 43 (1959).

³ K. L. Rinehart and R. J. Curby, J. Amer. Chem. Soc. **79**, 3290 (1957).

demonstrated.

Treatment of the ketone (I; $n = 3$) (250 mg) with (-)-menthydrazide according to Woodward et al.⁴ gave orange crystals of the (+)-ketone-(-)-menthydrazone (80 mg), m.p. 195-196° (vacuum sealed tube); $[\alpha]_D^{15} + 850^\circ \pm 5^\circ$ (c , 0.3 in CHCl_3) (Found: C, 66.8; H, 7.8; N, 6.7. $\text{C}_{25}\text{H}_{34}\text{FeN}_2\text{O}_2$ requires: C, 66.7; H, 7.6; N, 6.2%). The mother liquors from the reaction mixture yielded a small amount (12 mg) of impure (-)-ketone-(-)-menthydrazone, m.p. 193-196° (vacuum sealed tube); $[\alpha]_D^{15} - 350^\circ$ (c , 0.35 in CHCl_3). Acid hydrolysis⁴ of the (+)-ketone-(-)-menthydrazone (60 mg) followed by chromatography on alumina and repeated sublimation of the product at 110-120°/2mm gave the (+)-ketone (8 mg), m.p. 83-85° (lit.³ racemate m.p. 85.4-85.7°); $[\alpha]_D^{15} + 550^\circ$ (still increasing) (c , 0.3 in CHCl_3) (Found: C, 66.5; H, 5.9. Calc. for $\text{C}_{14}\text{H}_{14}\text{FeO}$: C, 66.2; H, 5.6%).

⁴ R. B. Woodward, T. P. Kohman and G. C. Harris, J. Amer. Chem. Soc., 63, 120 (1941).