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FERROCENYLKETENIMINE

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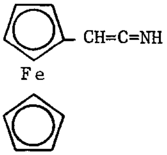
A number of N-substituted ketenimines have been reported in the literature (1-5). Dicyanoketenimine (6) is the only reported example having no N-substituent, but it is unstable at room temperature. This communication is concerned with the preparation and characterization of ferrocenylketenimine, the first reported example of a stable ketenimine which is unsubstituted at nitrogen.



Treatment of ferrocenylacetonitrile with methylmagnesium chloride in ether and subsequent addition of methanol gave ferrocenylketenimine, m.p. 144-147°, in 51% yield. The ketenimine structure is supported by spectral data and elemental analysis (Calculated for $C_{12}H_{11}FeN$: C, 64.03; H, 4.93; N, 6.22. Found: C, 64.10; H, 4.99; N, 5.93). The infrared spectrum showed strong N-H absorptions at 3450, 3320, 3240, and 3200 cm^{-1}, and a strong ketenimine absorption (1,2) at 2185 cm^{-1}.* The n.m.r. spectrum ($CDCl_3$) had a singlet at 3.56 p.p.m. (1H), a multiplet centered at 4.18 p.p.m. (9H), and a broad singlet at 4.75 p.p.m. (1H). The former singlet was assigned to the olefinic C-H and corresponds closely to those of vinylferrocene and 1,1'-divinylferrocene (3.51 and 3.59 p.p.m., respectively (7)). The positions of the imine-(latter singlet) and ring-proton absorptions are in agreement with published values. (8)

Generation of the ketenimine structure using bases other than Grignard reagents has met with little success. For example, the infrared spectrum of the product resulting from

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* This is an extraordinarily large shift from 2002-2016 cm^{-1} reported for aromatic ketenimines. (1)

treatment of ferrocenylacetonitrile with n-butyllithium in ether and subsequent neutralization with methanol showed only a weak ketenimine band at 2185 cm^{-1}. Reaction of the nitrile with methylsulfinyl carbanion (9) in dimethyl sulfoxide, followed by treatment with methyl iodide, resulted only in C-alkylation.

The effect of the ferrocene moiety in stabilizing the ketenimine structure is remarkable, and isomerization to ferrocenylacetonitrile has not been observed. There was no change in the infrared spectrum of a sample of ferrocenylketenimine after it had been heated to its melting point, and the crystalline material has been stored at room temperature for weeks with no change in its spectrum.

The preparation and chemistry of ferrocenylketenimine are under further investigation.

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