

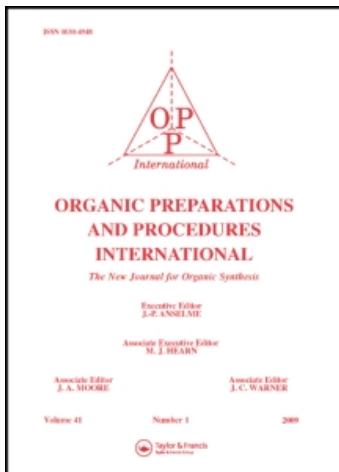
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1,1'-DIACETYLFERROCENE MONOTOSYLHYDRAZONE AND 1,1'-DIACETYLFERROCENE DITOSYLHYDRAZONE

Howard Alper^a; Susan J. Brown^a; Kenneth P. Jaffe^a

^a Department of Chemistry, State University of New York, Binghamton, New York

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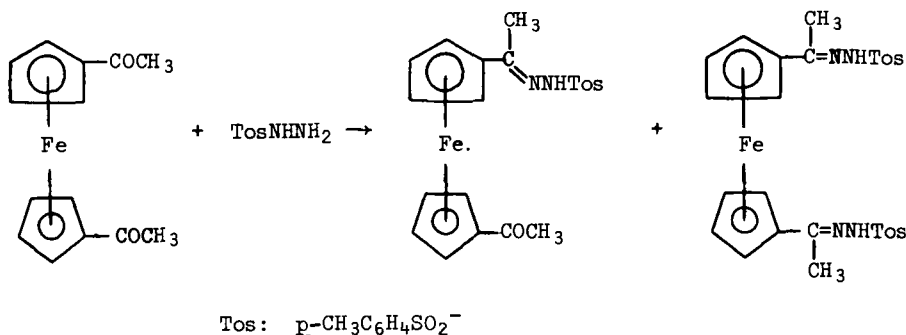
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1,1'-DIACETYLFERROCENE MONOTOSYLHYDRAZONE AND
1,1'-DIACETYLFERROCENE DITOSYLHYDRAZONE

Howard Alper, Susan J. Brown, and Kenneth P. Jaffe
Department of Chemistry, State University of New York
Binghamton, New York 13901



We wish to report the preparation of 1,1'-diacetylferrocene monotosylhydrazone and 1,1'-diacetylferrocene ditosylhydrazone. These compounds may prove to be valuable precursors to a number of novel ferrocenes.

A mixture of the mono- and ditosylhydrazones was prepared by reaction of 1,1'-diacetylferrocene with 1.5 equivalents of p-toluenesulfonylhydrazine in ethanol. The two products were easily separated by taking advantage of their solubility differences in chloroform-ethanol. The ditosylhydrazone can be obtained as the sole product by using a 1:2 mole ratio of 1,1'-diacetylferrocene to p-toluenesulfonylhydrazine.

EXPERIMENTAL

1,1'-Diacetylferrocene Monotosylhydrazone and 1,1'-Diacetylferrocene Ditosylhydrazone. To a solution of 2.79 g. (15 mmoles) of *p*-toluenesulfonylhydrazine in 13 ml. of warm absolute ethanol was added a warm solution of 2.70 g. (10 mmoles) of 1,1'-diacetylferrocene¹ in 35-40 ml. of absolute ethanol. The mixture was refluxed for 30 minutes, cooled to room temperature and filtered to give 4.70 g. of an orange-brown solid. The solid was treated with 60-70 ml. of a hot chloroform-ethanol (7:3) solution, filtered and the filtrate allowed to cool to room temperature whereupon the monotosylhydrazone precipitated. On filtration, 1,1'-diacetylferrocene monotosylhydrazone (1.11 g., 25%) was obtained as an orange-brown powder, m.p. 196-199° (dec.). The following infrared spectral bands (KBr disc) are noteworthy: 3275 [w, ν NH], 1645 [s, ν CO and ν C=N], 1609, 1598, 1493 [w-m, phenyl nucleus], 1338 [s, ν_{AS} SO₂], 1173, 1168 [s, doublet, ν_S SO₂], 1117 [m, acetyl group], 892, 879 [m, C-H bending mode on ferrocene ring] and 817 cm⁻¹ [m, out-of-plane bending for two adjacent hydrogens on the benzene] (w = weak, m = medium, s = strong). The nmr spectrum (dimethylsulfoxide-d₆) showed the following bands: 2.07 [singlet, $\underline{\text{CH}_3\text{C}=\text{N}-}$], 2.20 [singlet, $\underline{\text{CH}_3\text{CO}-}$], 2.47 [singlet, $\underline{\text{p-CH}_3\text{C}_6\text{H}_4-}$], 3.47 [broad singlet, NH], 4.45 [unsymmetrical triplet, H_{3,4} of cyclopentadienyl rings], 4.70 [unsymmetrical triplet, H_{2,5} of cyclopentadienyl rings], 7.60 and 8.03 ppm [AB quartet (J_{AB} = 25 cps) assigned to the four protons meta and ortho, respectively, to the sulfonyl group].

Anal. Calcd. for C₂₁H₂₂FeN₂O₃S: C, 57.54; H, 5.06; N, 6.39; S, 7.31. Found: C, 57.29; H, 5.11; N, 6.32; S, 7.47.

The orange, chloroform-ethanol insoluble solid was identified as 1,1'-diacetylferrocene ditosylhydrazone (2.72 g., 48%) which decomposed above 203°. The following infrared spectral bands (KBr disc) are note-

1,1'-DIACETYLFERROCENE MONOTOSYLHYDRAZONE

worthy: 3260 [w-m, ν_{NH}], 1648 [w-m, $\nu_{\text{C=N}}$], 1600, 1496, 1487 [m, phenyl nucleus], 1330 [s, ν_{ASO_2}], 1168, 1161 [s, doublet, $\nu_{\text{S}_2\text{O}_2}$], 886 [m-s, C-H bending mode on ferrocene ring] and 815 cm^{-1} [m-s, out-of-plane bending for two adjacent hydrogens on the benzene ring]. The ditosylhydrazone was insufficiently soluble in common nmr solvents (CDCl_3 , DMSO-d_6 , $\text{C}_6\text{H}_6\text{-d}_6$) to obtain a satisfactory nmr spectrum.

Anal. Calcd. for $\text{C}_{28}\text{H}_{30}\text{FeN}_4\text{S}_2\text{O}_4$: C, 55.44; H, 4.98; N, 9.23; S, 10.57. Found: C, 55.39; H, 4.99; N, 9.44; S, 10.28.

1,1'-Diacetylferrocene Ditosylhydrazone. To a solution of 1.87 g. (10 mmoles) of *p*-toluenesulfonylhydrazine in 8.5 ml. of warm absolute ethanol was added a warm solution of 1.35 g. (5 mmoles) of 1,1'-diacetylferrocene in 18 ml. of absolute ethanol. The mixture was refluxed for a few minutes, cooled to room temperature and then allowed to stand overnight. Filtration gave 2.65 g. (87%) of the ditosylhydrazone.

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