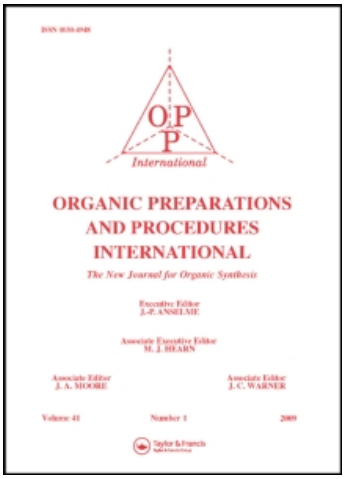

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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Howard Alper[a]; Susan J. Brown[a]; Kenneth P. Jaffe[a]
[a] Department of Chemistry, State University of New York, Binghamton, New York

To cite this Article Alper, Howard , Brown, Susan J. and Jaffe, Kenneth P.(1970) '1,1'-DIACETYLFERROCENE MONOTOSYLHYDRAZONE AND 1,1'-DIACETYLFERROCENE DITOSYLHYDRAZONE', Organic Preparations and Procedures International, 2: 3, 167 — 169
To link to this Article: DOI: 10.1080/00304947009458651
URL: http://dx.doi.org/10.1080/00304947009458651

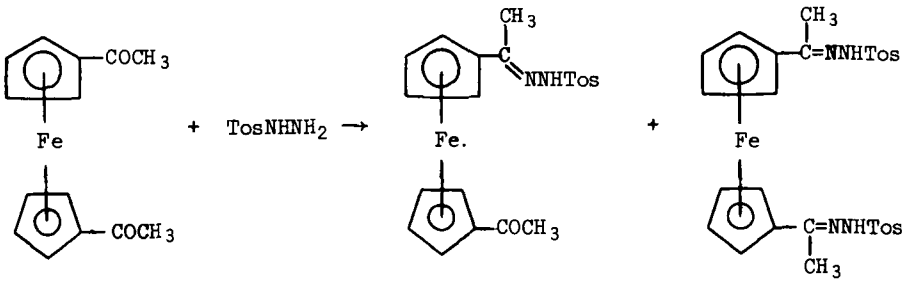
ORGANIC PREPARATIONS AND PROCEDURES 2(3), 167-169 (1970)

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



Tos: p-$CH_3C_6H_4SO_2^-$

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′-diacetylferrocene[1] 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, νNH], 1645 [s, νCO and νC=N], 1609, 1598, 1493 [w-m, phenyl nucleus], 1338 [s, $\nu_{AS}SO_2$], 1173, 1168 [s, doublet, $\nu_{S}SO_2$], 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-d_6) showed the following bands: 2.07 [singlet, $\underline{CH_3}C{=}N^-$], 2.20 [singlet, $\underline{CH_3}CO^-$], 2.47 [singlet, p-$\underline{CH_3}C_6H_4^-$], 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 $C_{21}H_{22}FeN_2O_3S$: 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-

worthy: 3260 [w-m, νNH], 1648 [w-m, νC=N], 1600, 1496, 1487 [m, phenyl nucleus], 1330 [s, $\nu_{AS}SO_2$], 1168, 1161 [s, doublet, $\nu_{S}SO_2$], 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, C_6H_6-d_6) to obtain a satisfactory nmr spectrum.

Anal. Calcd. for $C_{28}H_{30}FeN_4S_2O_4$: 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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(Received January 20, 1970)