Ferrocenylidene Hydrazides

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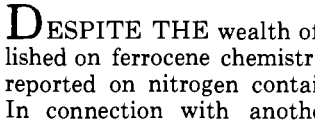
DESPITE THE wealth of material which has been published on ferrocene chemistry (*1*) relatively little has been reported on nitrogen containing derivatives of ferrocene. In connection with another problem, which we have temporarily had to abandon, it was necessary to prepare a number of ferrocenylidene hydrazides (I). These compounds (I), shown in Table I, were readily prepared by refluxing crude ferrocenecarboxaldehyde (II) and the appropriate hydrazide in absolute ethanol. For comparision purposes it was also desirable to have on hand the corresponding benzylidene hydrazides (III). All of



I X = N—NH—COR

II X = O

III $C_6H_5CH=N—NH—COR$

these have been previously reported in the literature with the exception of the compound (III, R = cyclopropyl) derived from cyclopropanecarboxhydrazide which is also included in Table I.

The infrared spectra (KBr discs) of the ferrocenylidene and benzylidene hydrazides exhibited little difference in the —NH stretching mode (3230–3150 $cm.^{-1}$) and carbonyl absorption (1673–1635 $cm.^{-1}$). As expected all of the ferrocenylidene hydrazides had peaks at 1110–1102 $cm.^{-1}$ and 1005–998 $cm.^{-1}$. In the ultraviolet (95% ethanol) the benzylidene hydrazides exhibited maxima at 212–220 mμ. ($\epsilon_{avg.}$ = 25,000) and 280–300 mμ. ($\epsilon_{avg.}$ = 28,500) while the ferrocenylidene hydrazides exhibited three maxima at 207–209 mμ. ($\epsilon_{avg.}$ = 30,500), 250–260 mμ. ($\epsilon_{avg.}$ = 23,900), and 293–304 mμ. ($\epsilon_{avg.}$ = 27,000). The compound I (R = *o*—HO—C_6H_4—), however, exhibited maxima only at 210 and 317 mμ.

The benzylidene hydrazide (III, R = ferrocenyl) from benzaldehyde and ferrocenecarboxhydrazide was also prepared and is included in Table I.

EXPERIMENTAL

Reagents. All hydrazides were obtained commercially with the exception of ferrocenecarboxhydrazide which was prepared by refluxing ethyl ferrocenecarboxylate with 95% hydrazine. Ferrocenecarboxaldehyde was prepared by essentially the same method as described by Pauson (*2*).

Ferrocenylidene hydrazides. A mixture of 0.005 moles of ferrocenecarboxaldehyde and 0.0055 moles of the appropriate hydrazide was refluxed in absolute ethanol for 15 mins. The mixture was allowed to stand overnight and if the ferrocenylidene hydrazides had not separated they were precipitated by the addition of water. The products were then recrystallized from aqueous ethanol to give the materials shown in Table I. The two benzylidene hydrazides reported in Table I as well as the other, previously reported, hydrazides of this type were prepared by a similar method except that a slight excess of benzaldehyde was used.

LITERATURE CITED

(1) Plesske, K., *Angew. Chem. int. edn.* **1**, 312, 394 (1962).
(2) Pauson, P.L., *J. Chem. Soc.* **1958**, p. 650.

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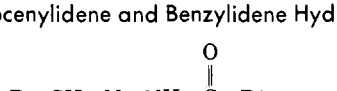
Table I. Ferrocenylidene and Benzylidene Hydrazides



R	R′	M.p., °C.	Yield, %	Analysis[a] Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
$C_5H_5FeC_5H_4$—	C_6H_5—	186–187	83	65.08	4.86	8.43	65.38	5.14	8.63
$C_5H_5FeC_5H_4$—	*p*-CH_3—C_6H_4—	216	98	65.88	5.21	8.09	65.50	5.43	8.25
$C_5H_5FeC_5H_4$—	*o*—HO—C_6H_4—	208	55	62.15	4.59	8.05	62.16	5.01	7.76
$C_5H_5FeC_5H_4$—	$(C_6H_5)_2$—C(OH)—	195–200	96	68.50	5.03	6.39	68.88	5.49	6.58
$C_5H_5FeC_5H_4$—	CH_3—	196–197	69	57.79	5.22	10.37	57.62	5.36	10.39
$C_5H_5FeC_5H_4$—	NC—CH_2—	185–186	79	56.95	4.41	14.25	56.66	4.67	14.25
$C_5H_5FeC_5H_4$—	cyclopropyl-	208–209	55	60.83	5.45	9.46	61.09	5.41	9.76
$C_5H_5FeC_5H_4$—	—$(CH_2)_5$—	143–145	62	59.85	5.50	9.63	60.44	6.11	9.76
C_6H_5—	cyclopropyl-	152	99	70.42	6.39	14.90	70.45	6.58	14.81
C_6H_5—	$C_5H_5FeC_5H_4$—	187–188	69	65.08	4.86	8.43	65.19	5.04	8.38