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CONFIGURATIONS OF PSEUDOASYMMETRIC FERROCENES

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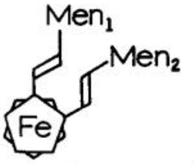
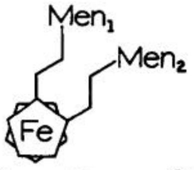
We recently reported experimental demonstrations of previously unknown pseudoasymmetric ferrocenes:[1] 1A, 2A and 1B and 2B were shown to be achiral (optically inactive) and diastereomerically related to each other and to each of the two chiral (optically active) members, 3A, 4A and 3B, 4B, in each set.

Set A

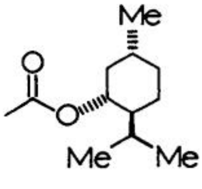


Set B

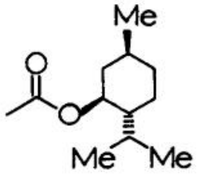


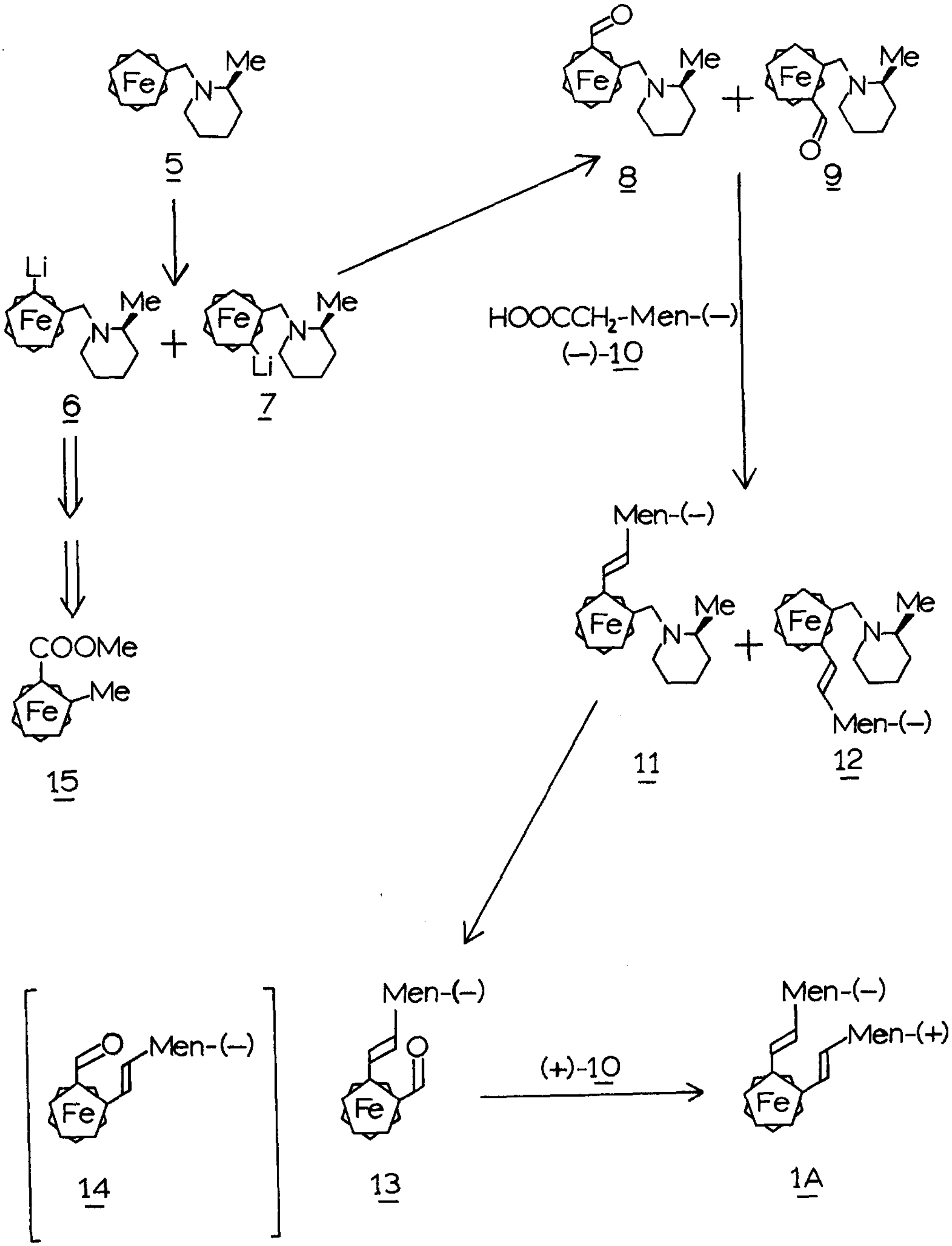
Isomer	Men_1	Men_2	mp °C	$[\alpha]_D$	Isomer	Men_1	Men_2	mp °C	$[\alpha]_D$
1A	(-)	(+)	146-8	0	1B	(-)	(+)	liq	0
2A	(+)	(-)	174-5	0	2B	(+)	(-)	116-8	0
3A	(+)	(+)	144-6	+70.0±1.2	3B	(+)	(+)	liq	+56.3±1.0
4A	(-)	(-)	144-6	-72.3±2.0	4B	(-)	(-)	liq	-54.2±0.9

Men-(–) =



Men-(+) =




Fe
Me
5
Li
6
7
8
9
HOOCCH$_2$-Men-(–)
(–)-10
11
12
Men-(–)
COOMe
15
Men-(–)
14
13
(+)-10
Men-(+)
1A

We now report results that provide unequivocal assignments of configuration to each of the *pseudo*asymmetric ferrocenes.

Lithiation of (+)-(*S*)-*N*-ferrocenylmethyl-2-methylpiperidine (5) with *n*-butyllithium takes place stereoselectively [2,3] to give a mixture of the two diasteriomeric lithio compounds, 6 and 7, with the former predominating. Conversion of this mixture to the corresponding mixture of formyl compounds, 8 and 9[4], was accomplished in 92% yield by treatment with *N*,*N*-dimethylformamide. Modified Knoevenagel condensation[1] with (-)-carbomenthoxyacetic acid [(-)-10] gave a mixture of 11 and 12 in 90% yield, which was separated by chromatographic methods: the predominant diastereomer (11)[4], a red oil with $[\alpha]^{19}_{D}$ + 770 ± 8° (*c* 0.500, ethanol), made up 79% of the mixture, while the minor isomer (12)[4], also a red oil with $[\alpha]^{19}_{D}$ - 643 ± 24° (*c* 0.330, ethanol), was 21% of the mixture[5].

The predominant isomer (11) was oxidized with activated magnanese dioxide to 13, previously prepared and characterized in combination with its diastereomer (14).[1] Condensation of 13 with (+)-10 gave the *pseudo*asymmetric compound (1A), identical in all respects with the lower-melting *pseudo*asymmetric isomer of Set A. Designation of this material as 1A (not 1B) rests on the previous correlation[2] of the predominant lithio diastereomer (6) with the levorotatory ester (15) whose absolute configuration was secured recently[6] through correlation with an X-ray established standard[7]. Thus, with configurational assignments to the *pseudo*asymmetric pair of diastereomers, 1A and 2A, of Set A made, assignments to the corresponding pair, 1B and 2B, of Set B follow since each of the latter were obtained directly from the former[1].

References

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4. All new compounds give satisfactory analyses.

5. Double bond configurations for these compounds, as well as for the other olefinic compounds of the entire study[1], are all (E) as consistently shown by the 16 Hz spacings of the AB pattern owing to the vinylic protons.

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