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# PREPARATION AND SYNTHETIC UTILITY OF 2-(CHLOROMERCURI)[(DIMETHYLAMINO)METHYL]FERROCENE

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## SUMMARY

2-(Chloromercuri)[(dimethylamino)methyl]ferrocene I has been successfully synthesized from 2-lithio[(dimethylamino)methyl]ferrocene II and 2-[(dimethylamino)methyl]ferroceneboronic acid III. Chloromercuri-amine I was transmetalated to give improved yields of 2-lithio-amine II. Chloromercuri-amine I was readily converted to 2-iodo[(dimethylamino)methyl]ferrocene V. The PMR spectrum of chloromercuri-amine I served to extend the concept of a contact interaction between the 2-substituent and the adjacent diastereotopic methylene protons.

Recent interest in the preparation of 1,2-substituted derivatives of ferrocene using a directed 2-lithiation technique* prompts us to report our successful synthesis of 2-(chloromercuri)[(dimethylamino)methyl]ferrocene (I). This compound is representative of a novel class of $\sigma,\pi$-bimetallic organometallic compounds and also offers a potentially useful isolable intermediate for the synthesis of 1,2-disubstituted ferrocenes**.

Chloromercuri-amine (I) was conveniently prepared by two separate procedures (Scheme 1). One route involved transmetalation of 2-lithio[(dimethylamino)methyl]ferrocene (II)[3] using an excess of solid mercuric chloride. In the other, 2-[(dimethylamino)methyl]ferroceneboronic acid (III)[4] was converted into chloromercuri-amine (I) by treatment with mercuric chloride in acetone. The two methods gave comparable yields. Elemental analysis and spectral data supported the proposed structure. IR bands at approximately 9 and 10 $\mu$ demonstrated the homoannular substitution[5] pattern of the compound; a band at 9.35 $\mu$ afforded tentative proof of the 1,2-disposition of the substituents***. Confirming evidence for the 1,2-relationship of the substituents was forthcoming from the observance of nonequivalent methylene protons in the PMR spectrum of the compound[6].

The PMR spectrum of chloromercuri-amine (I) deserves further comment

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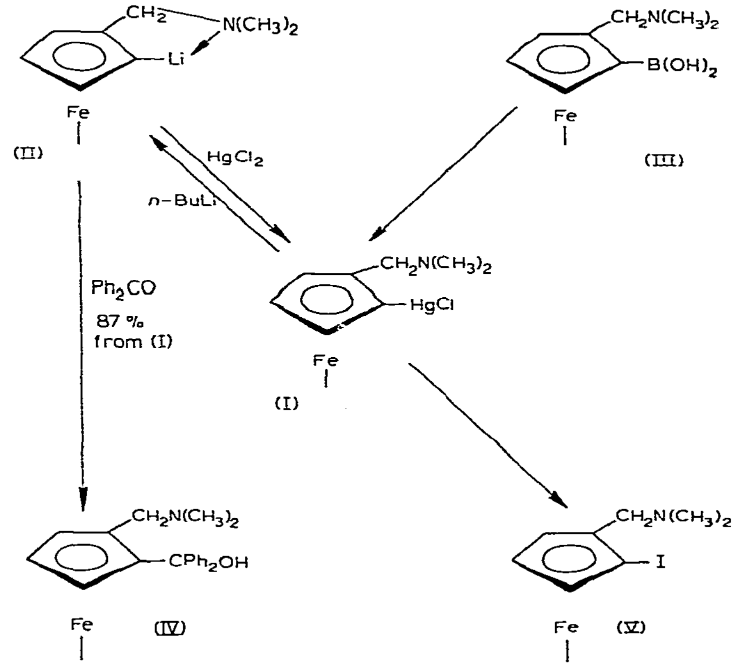
* For a recent review which includes a comprehensive coverage of 2-metalation of substituted ferrocenes, *cf.* ref. 1.

** Some transformations of (chloromercuri)ferrocene itself have been reported, *cf.* ref. 2.

*** This medium intensity band has appeared between 9.2 and 9.45 $\mu$ in all 1,2-disubstituted ferrocenes prepared in this laboratory with the exception of those possessing functional group absorption in this region. Details of this observation are to be reported in forthcoming communication.

since the chloromercuri group is a member of a group of substituents known to be cylindrically symmetrical. Thus, the chloromercuri group presents an interesting example of contact influence on the nonequivalent methylene protons similar to that reported for the 2-halo[(dimethylamino)methyl]ferrocenes[7]. For 2-chloromercuri-amine (I) the difference in chemical shift ($\delta_{AB}$) of the methylene protons in $CDCl_3$ is 25.0 Hz with a $J_{AB}$ of 14.1 Hz, the $\delta_{AB}$ being more than twice that observed when Cl was the substituent (9.6 Hz in $CDCl_3$). A recent paper[8] indicates that the $A$ value of Cl is only slightly greater than that for HgCl. However, the electron density surrounding the metal atom is greater than that in the Cl substituent and results in the larger $\delta_{AB}$ value in accord with the proposed contact interaction.

SCHEME 1



Chloromercuri-amine (I) can be transmetalated with n-butyllithium to give 87.3% 2-lithio[(dimethylamino)methyl]ferrocene (II) as indicated by the yield of benzophenone condensation product (IV). This represents an increase in yield of 15.3% compared to that from the direct lithiation of [(dimethylamino)methyl]-ferrocene[3]. (I) is also smoothly converted into 2-iodo-amine (V) by treatment with iodine in xylene. The 2-carbinol-amine (IV) and 2-iodo-amine (V) proved to be identical to authentic samples prepared from 2-lithio-amine (II)[3] and from 2-boronic acid (III)[4], respectively. The respective samples gave identical m.p.'s, mixed m.p.'s and IR spectra.

## EXPERIMENTAL

Elemental analyses were performed by Galbraith Laboratories, Nashville, Tennessee. Melting points were determined on a Hoover melting point apparatus and were corrected. The NMR spectra were run on a Varian A-56/60 spectrometer using TMS as an internal standard. All IR spectra were determined as Nujol mulls on a Perkin–Elmer Model 137 Infracord spectrometer.

*Preparation of 2-(chloromercuri)[(dimethylamino)methyl]ferrocene (I) from lithioamine (II)*

Under a stream of nitrogen, [(dimethylamino)methyl]ferrocene (4.86 g, 20 mmoles) in ether was treated with n-butyllithium (50 mmoles) at room temperature for 2 h[3]. Solid mercuric chloride (13.6 g, 50 mmoles) was added. The solution was light orange at this point. Five min later the reaction mixture began to reflux and subsequently turned dark green. After 1½ h, the reaction solution was treated with water (25 ml) and stirred overnight. The contents were scraped into a beaker and washed with benzene until the decanted benzene was colorless. The benzene extracts were filtered and stripped to dryness. Mercuric chloride was largely removed from the solid residue by dissolving the residue in chloroform, adding petroleum ether until a white precipitate formed, and then filtering. After stripping solvent from the filtrate, final traces of mercuric chloride were removed by washing the solid with a saturated sodium chloride solution. Yield 72%; m.p. 125.5–126.5°. (Found: C, 32.43; H, 3.33; Cl, 7.20; Fe, 11.39; Hg, 42.19; N, 2.80; $C_{13}H_{16}ClFeHgN$ calcd.: C, 32.65; H, 3.37; Cl, 7.41; Fe, 11.68; Hg, 41.95; N, 2.92%.) NMR ($CDCl_3$): $\tau$ 7.73 (s, $CH_3$); $\tau$ 7.07, 6.83, 6.50, 6.27 (AB quartet, $CH_2$), $\tau$ 5.88 (bs, $C_5H_5$ + one proton of substituted cyclopentadienyl ring); $\tau$ 5.70 (m, two protons of substituted cyclopentadienyl ring); overall ratio 6/2/6/2, respectively.

*Preparation of 2-(chloromercuri)[(dimethylamino)methyl]ferrocene (I) from [(dimethylamino)methyl]ferroceneboronic acid (II)*

In a dry one-liter flask, 2-boronic acid (II) (5.0 g, 17.5 mmoles) was dissolved in 400 ml of refluxing acetone. Mercuric chloride (4.75 g, 17.5 mmoles) dissolved in 100 ml of acetone was added rapidly and the refluxing solution was stirred for 15 min. The acetone solution was concentrated to approximately 50 ml and filtered through a fritted buchner funnel. After being washed with petroleum ether, ethyl ether, and 50 ml of methylene chloride, the solid was scraped into 100 ml of 10% sodium hydroxide and extracted with ether. The ethereal extracts were dried over magnesium sulfate and stripped to dryness. The oil was taken up in light petroleum ether from which the product was allowed to crystallize, m.p. 125.5–126.5°, 3.05 g (64%).

*Transmetalation of chloromercuri-amine (I) with n-butyllithium*

Under a stream of nitrogen, chloromercuri-amine (I) (0.328 g, 0.674 mmoles) in ether was treated with n-butyllithium (0.787 mmoles) at room temperature for 1 h. Benzophenone (0.178 g, 1.00 mmole) in ether was added and the resulting solution was stirred overnight. After hydrolysis with water, the reaction products were extracted with ether, concentrated to an oil, and placed on an alumina III chromatography column. 5% Ether in benzene eluted carbinol-amine (IV), 0.241 g, 87.3%, m.p. 121–125° (lit.[3] m.p. 121–125°).

*2-Iodo[(dimethylamino)methyl]ferrocene (V)*

Chloromercuri-amine (I) (1.00 g, 2.09 mmoles) was stirred with iodine (2.0 g

7.9 mmoles) in xylene (20 ml) at room temperature for 1 h. The reaction mixture was extracted with three 100-ml portions of 10% sodium thiosulfate, dried over magnesium sulfate and reduced to an oil under high vacuum. The oil was chromatographed on alumina III. The first fraction was eluted with petroleum ether and stripped to dryness. Re-crystallization from pentane on a dry-ice cake gave iodo-amine (V), 0.309 g, 40%, m.p. 28° (lit.[4] m.p. 28–28.5°). IR and NMR spectra were identical to those of an authentic sample.

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