

## FERROCENYLMETHYL AZIDE

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(Received December 12th, 1969)

### SUMMARY

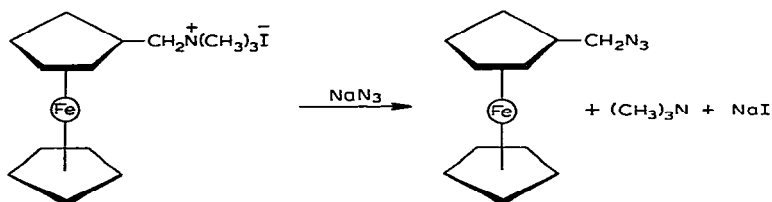
The preparation of ferrocenylmethyl azide and its use as a synthetic intermediate is discussed. Acid catalyzed decomposition of the azide provides the novel product bis(ferrocenylmethyl)amine.

### INTRODUCTION

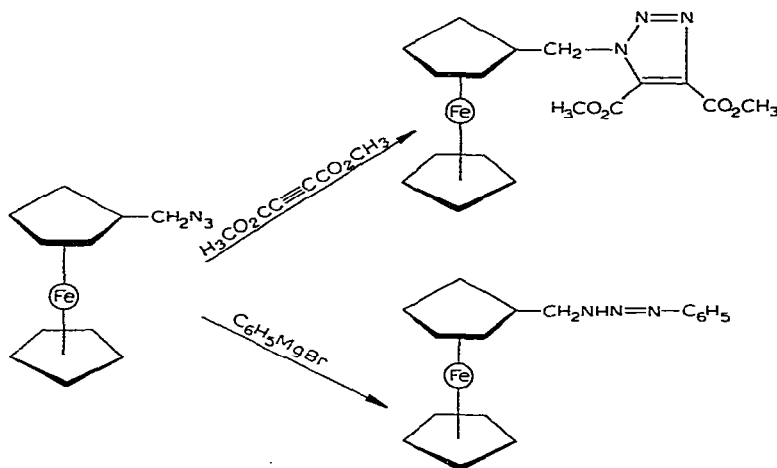
[(Dimethylamino)methyl]ferrocene methiodide has been shown to be an extremely useful intermediate in the preparation of many ferrocene containing compounds. When this quaternary salt is treated with any one of a variety of nucleophilic agents, a facile displacement of trimethylamine occurs resulting in the formation of a ferrocenylmethyl substituted compound<sup>1,2</sup>. One of these compounds, the previously unknown ferrocenylmethyl azide, has provided an important, reactive intermediate.

### RESULTS AND DISCUSSION

Treatment of an aqueous solution of [(dimethylamino)methyl]ferrocene methiodide with sodium azide, results in its conversion to ferrocenylmethyl azide as shown below. Concomitantly, ferrocenecarboxaldehyde and ferrocenemethanol are formed in the reaction. Separation of these minor by-products from the desired azide may be readily accomplished by chromatography on a short column of alumina.



Ferrocenylmethyl azide undergoes a 1,3-dipolar addition reaction with dimethyl acetylenedicarboxylate in carbon tetrachloride to form dimethyl 1-(ferrocenylmethyl)-1,2,3-triazole-4,5-dicarboxylate. Reaction of the azide with phenylmagnesium



bromide produces the 1,3-addition product 1-(or 3)-(ferrocenylmethyl)-3-(or 1)-phenyltriazene.

Reduction of ferrocenylmethyl azide by a standard method using lithium aluminum hydride in ether<sup>3</sup> proceeds smoothly with simultaneous evolution of nitrogen to provide (ferrocenylmethyl)amine in near quantitative yield.

The behavior of ferrocenylmethyl azide under conditions of acid catalyzed decomposition does not follow the pattern previously established for ( $\alpha$ -ferrocenyl)-benzyl azide<sup>4</sup>. The decomposition products of the latter azide are 1,2-diferrocenyl-1,2-diphenylethane and ferrocenecarboxaldehyde. In the decomposition of ferrocenylmethyl azide none of the expected dimerization product, 1,2-diferrocenylethane is observed. The only isolable products were bis(ferrocenylmethyl)ether, ferrocenecarboxaldehyde, and the previously unknown bis(ferrocenylmethyl)amine, in addition to a trace of unidentifiable material. The structure of bis(ferrocenylmethyl)amine was proven by its synthesis via *N*-(ferrocenylmethyl)ferrocenecarboxamide and reduction with lithium aluminum hydride.

The availability of [(dimethylamino)methyl]ferrocene methiodide, the ease with which it can be converted to ferrocenylmethyl azide and subsequently reduced to (ferrocenylmethyl)amine makes this an attractive alternate route in the synthesis of the last compound. A second method utilized the reaction of [(dimethylamino)-methyl]ferrocene methiodide, the same starting material employed in the present study, with potassium phthalimide. Reaction of the resulting *N*-substituted phthalimide with hydrazine hydrate formed the desired amine in 65–70% yield from the quaternary salt<sup>5</sup>. Although this new method shows no advantage over the phthalimide method from the standpoint of either yield or convenience, it does provide the new useful intermediate, ferrocenylmethyl azide.

## EXPERIMENTAL

All melting points were determined on a Kofler Heizbank previously calibrated in the region of the melting point obtained. A Varian A-60 nuclear magnetic spectrometer and Beckman IR-5 spectrophotometer were used to obtain the respective spectra.

### Preparation of ferrocenylmethyl azide

A mixture comprised of 23.0 g (0.06 mole) of [(dimethylamino)methyl]ferrocene methiodide, 23.0 g (0.35 mole) of sodium azide, and 230 ml of water was maintained at reflux for 6 h then allowed to cool. The solution was repeatedly extracted with ether and the combined ether extracts dried over anhydrous magnesium sulfate. The ether solution was filtered and evaporated *in vacuo*. The residual orange oil was taken up in hexane and chromatographed on a column of Alcoa F-20 alumina (activity grade III)<sup>6</sup>. Elution with hexane provided, after evaporation of the solvent, 9.0 g (62%) of ferrocenylmethyl azide as an orange solid (m.p. 32–34°). IR absorption (neat) at 3.27  $\mu$  (CH), 3.50  $\mu$  (CH), 4.80  $\mu$  (N<sub>3</sub>), 9.03  $\mu$  and 10.0  $\mu$  (unsubstituted ring) and NMR peaks (CCl<sub>4</sub>) at  $\delta$  4.13 (multiplet) confirmed the structure. (Found: C, 54.7; H, 4.8; N, 17.2. C<sub>11</sub>H<sub>11</sub>FeN<sub>3</sub> calcd.: C, 54.8; H, 4.6; N, 17.4%.)

Elution with 20% ether/hexane removed 0.2 g (2%) of ferrocenecarboxaldehyde. A further change of eluent to 50% ether/hexane removed 1.1 g (8.6%) ferrocenemethanol. The last two compounds were identified by means of their IR spectra and melting points.

### Reaction of ferrocenylmethyl azide with dimethyl acetylenedicarboxylate

A solution of 5.0 g (0.021 mole) of ferrocenylmethyl azide and 2.8 g (0.021 mole) of dimethyl acetylenedicarboxylate in 25 ml of carbon tetrachloride was maintained at reflux under argon for 5 h. The solution was evaporated *in vacuo* and the residue recrystallized from ethanol to give 5.0 g (64%) dimethyl 1-(ferrocenylmethyl)-1,2,3-triazole-4,5-dicarboxylate (m.p. 92°), identified by means of its IR and NMR spectra in conjunction with microanalytical data. (Found: C, 52.75; H, 4.79; N, 11.30. C<sub>17</sub>H<sub>17</sub>FeN<sub>3</sub>O<sub>4</sub> calcd.: C, 53.28; H, 4.47; N, 10.96%.)

### Reduction of ferrocenylmethyl azide with lithium aluminum hydride [(ferrocenylmethyl)amine]

To a stirred solution of 5.0 g (0.13 mole) of lithium aluminum hydride in 400 ml of ether there was added dropwise under nitrogen a solution of 10.0 g (0.04 mole) of ferrocenylmethyl azide in 100 ml ether. The mixture was then stirred at reflux for 2 h, cooled and hydrolyzed by careful dropwise addition of 200 ml water. The ether phase was separated, dried over anhydrous magnesium sulfate, filtered and evaporated *in vacuo* to give 8.8 g (99%) of the previously known<sup>5</sup> (ferrocenylmethyl)amine ( $n_D^{25}$  1.6420). The structure of the compound was confirmed by means of its IR and NMR spectra.

### 1-(or 3)-(Ferrocenylmethyl)-3-(or 1)-phenyltriazine

To a stirred solution of 5.0 g (0.22 mole) of ferrocenylmethyl azide in 200 ml of dry ether was added dropwise a solution of 0.025 mole of phenylmagnesium bromide in 100 ml of ether. The reaction mixture was maintained at reflux for 2 h, then cooled and hydrolyzed with water. The ether phase was separated, dried, and evaporated *in vacuo*. The residual solid was washed with hexane and dried to give 3.7 g (56%) of 1-(or 3)-(ferrocenylmethyl)-3-(or 1)-phenyltriazine (m.p. 105°) identified by means of its IR and NMR spectra. In other experiments, the presence of small amounts of benzylferrocene was detected.

*Acid catalyzed decomposition of ferrocenylmethyl azide*

To a stirred solution of 0.9 g of ferrocenylmethyl azide in 20 ml of dry chloroform there was added, all at once, 10 ml of concentrated sulfuric acid. The mixture was stirred for 20 min during which time the nitrogen evolution ceased. The mixture was poured over ice and reduced with ascorbic acid. The aqueous phase was separated and washed twice with chloroform. The combined chloroform extracts were dried with anhydrous magnesium sulfate and evaporated to dryness. The residue was taken up in a minimal amount (ca. 2 ml) of benzene and placed on a column of activity grade III alumina. No material was removed using hexane as eluent; a change of eluent to 2% ether/hexane removed bis(ferrocenylmethyl)ether while 5% ether/hexane removed ferrocene carboxaldehyde. Identification of these materials was based on their IR spectra and melting point data. When the eluent was changed to 20% ether/hexane the major band was removed. The compound, an orange solid (m.p. 117.0–118.5), was identified as bis(ferrocenylmethyl)amine by means of its IR and NMR spectra. An analytical sample was prepared by sublimation at 140–145°/0.1 mm. (Found: C, 63.56; H, 5.58; N, 3.78.  $C_{22}H_{23}Fe_2N$  calcd.: C, 63.96; H, 5.61; N, 3.39%.)

The material was identical in all respects to that obtained by lithium aluminum hydride reduction of *N*-(ferrocenylmethyl)ferrocenecarboxamide [from (ferrocenylmethyl)amine and ferrocenoyl chloride; m.p. 208–210°].

## REFERENCES

- 1 D. E. BUBLITZ AND K. L. RINEHART, JR., *Org. Reactions*, 17 (1969) 21.
- 2 M. ROSENBLUM, *Chemistry of the Iron Group Metalloenes*, Part I, Interscience, 1965, p. 137.
- 3 J. H. BOYER, *J. Amer. Chem. Soc.*, 73 (1951) 5865.
- 4 A. BERGER, W. E. MCEWEN AND J. KLEINBERG, *J. Amer. Chem. Soc.*, 83 (1961) 2274.
- 5 A. N. NESMEYANOV, E. G. PEREVALOVA, L. S. SHILOVTSEVA AND V. D. TYURIN, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1962) 1997; *Chem. Abstr.*, 58 (1963) 9132.
- 6 G. HESSE, I. DANIEL AND G. WOHLLEBEN, *Angew. Chem.*, 64 (1952) 103.

*J. Organometal. Chem.*, 23 (1970) 225–228