

Notes

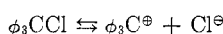
A department for short papers of immediate interest.

The Ferrocene Reduction of the Triphenylmethyl Carbonium Ion¹

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Received October 14, 1955

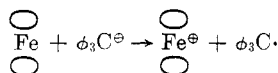
Due to the extreme ease with which ferrocene enters into one-electron transfer redox reactions,² it was of interest to briefly investigate the possible reduction of carbonium ions to stable free radicals through the agency of ferrocene. Triphenylmethyl chloride in nitromethane solution was chosen as a source of the model triphenylmethyl carbonium ion since the reversible equilibrium has been well estab-



lished³ in this solvent. The addition of a slight excess of ferrocene to these nitromethane solutions in the presence of oxygen immediately produced the green coloration of the ferricinium ion and a mild exotherm. Oxygen was absorbed by the solution and the immediate precipitation of di(triphenylmethyl)peroxide occurred. The latter material was isolated in only 16% yield and no significant quantity of ferrocene was recovered thus indicating the occurrence of side reactions such as attack of triphenylmethyl or the corresponding carbonium ion on ferrocene or the ferricinium ion. The only material isolated in addition to the peroxide was a mixture of solids which was not characterized.

A similar experiment was conducted in benzene solution and it was observed that no oxidation of the ferrocene occurred until a small quantity of phenol was added to the solution. The phenol presumably functioned as an electrophilic catalyst for the ionization of triphenylmethyl chloride.

It is thus established, in principle at least, that



the reaction will occur in polar, non-functional solvents.

EXPERIMENTAL

Pure triphenylmethyl chloride (800 mg., 2.9×10^{-3} mole, m.p. 110–111°) and 800 mg. of pure ferrocene (4.3×10^{-3} mole) were placed in a 50-ml. round-bottomed flask

(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) See Woodward, Roseblum, and Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952) for several examples.

(3) Smith and Leffler, *J. Am. Chem. Soc.*, **77**, 1700 (1955).

and 20 ml. of pure dry nitromethane was added while the flask was flushed with dry oxygen. The flask was immediately stoppered and shaken for one-half hour. On adding the solvent a mild exotherm occurred along with the green coloration of the ferricinium cation and the immediate precipitation of di(triphenylmethyl)peroxide. On opening the flask a considerable decrease in internal pressure was found to have occurred. Methylene chloride (100 ml.) was added and the organic layer was washed copiously with water to remove the intensely blue ferricinium salt. The organic layer was dried over sodium sulfate and was evaporated to dryness under a vacuum. The residual solid was extracted with pentane (which gave 150 mg. of ferrocene on evaporation), heated to boiling with acetone, and the white crystalline product was removed by filtration, yield 120 mg. (2.32×10^{-4} mole or 16%), m.p. 176–177°. The crude product was recrystallized from methylene chloride-pentane to a constant melting point of 184–185°⁴ and gave a positive test for peroxide by treatment with sodium iodide after decomposition in concentrated sulfuric acid followed by dilution with water.

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(4) Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900), reports a melting point of 185–186° for di(triphenylmethyl)peroxide.

The Preparation of Phthalyl Glycyl *dl*-β-(3,4-Dihydroxyphenyl)alanine Methyl Ester

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Received October 17, 1955

It was of interest to us to prepare peptides containing *dl*-β-(3,4-dihydroxyphenyl)alanine (Dopa). No peptides containing this amino acid have been reported in the literature. The synthesis methods of Bergmann,¹ Cook, *et al.*,² and of Sheehan and Frank³ were explored. Only the method of Sheehan and Frank was successful in our hands.

By a minor modification of the Sheehan and Frank method, phthalyl glycyl Dopa methyl ester, and its diacetate were successfully prepared. The presence of Dopa with both hydroxyl groups free in the final peptide was confirmed by the Arnov test.⁴

(1) Bergmann and Zervas, *Ber.*, **65**, 1192 (1932).

(2) Cook, Heilbron, and Levy, *J. Chem. Soc.*, 205 (1948).

(3) Sheehan and Frank, *J. Am. Chem. Soc.*, **71**, 1860 (1949).

(4) Arnov, *J. Biol. Chem.*, **118**, 531 (1937).