An Unusual Reaction of Ferrocenyl(trichloromethyl)- and Ferrocenyl(dichloromethyl)-methanol

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Summary The title compounds undergo an unusual elimination of the elements of HOCl on reaction with conc. H_2SO_4, and when their acetates are pyrolysed.

In the course of our investigation of the special stability of α-ferrocenylcarbonium ions[1] we observed that when a solution of ferrocenyl(trichloromethyl)methanol (Ia) in 98% H_2SO_4 was set aside for *ca.* 25 min and then poured over ice, work-up of the reaction mixture yielded *ca.* 90% of 1-ferrocenyl-2,2-dichloroethylene (IIa)† and *ca.* 10% of unchanged alcohol.‡

$$C_5H_5FeC_5H_4{\cdot}CH(OH)R^1 \xrightarrow[H_2O]{H^+} C_5H_5FeC_5H_4{\cdot}CH:CR^2R^3$$

(I) (II)

a; $R^1 = CCl_3$ a; $R^2R^3 = Cl_2$

b; $R^1 = CHCl_2$ b; $R^2R^3 = HCl$

The elements of HOCl were also eliminated under similar conditions from ferrocenyl(dichloromethyl)methanol (Ib) giving *trans*-1-ferrocenyl-2-chloroethylene,[2] *trans*-(IIb) (37%) and unchanged alcohol (16%).

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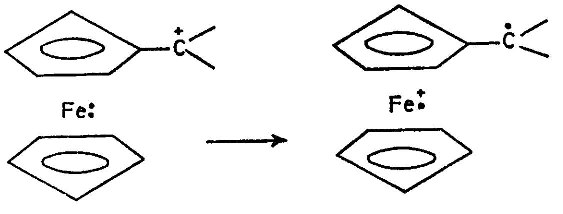
† With the tribromomethyl derivative, the yield of the dibromoethylene was *ca.* 56%, under similar conditions.

‡ All the compounds reported herein have been fully characterized by elemental analysis, i.r., u.v., n.m.r., and mass spectrometry and/or comparison with authentic samples.

To our knowledge there is no precedent concerning the elimination of the elements of HOCl from chlorohydrins under our reaction conditions.[3] In fact when we attempted[4] the same reaction procedure with phenyl(trichloromethyl)-methanol the only product isolated was the ether (PhCH·$CCl_3)_2O$. Further, ferrocenyl(chloromethyl)methanol was recovered quantitatively from a conc. sulphuric acid solution, attesting to the formation, in the acid medium, of a stable α-ferrocenylcarbonium ion of known type.[1]



(III) (IV)

Pyrolysis (160—200° at 0·1 mmHg) of the acetate of (Ia) yielded 43% of the gem-dichlorovinyl derivative (IIa) and pyrolysis (140° at 0·1 mmHg) of the acetate of (Ib) produced *ca.* 21% of the chlorovinyl compound (IIb) (and 27% of unchanged acetate). On the other hand the acetate derived from phenyl(trichloromethyl)methanol was quantitatively recovered unchanged on attempted pyrolysis. Whilst it is reasonable to consider a radical mechanism to explain the elimination of the elements of HOCl in the pyrolysis of the acetate derivatives of alcohols (Ia) and (Ib), there is little doubt that dissolving them in acidic media leads first to formation of the respective α-ferrocenylcarbonium ions (III).§

Subsequently, chlorine atom abstraction by a radical species such as (IV),[1] for which some spin-trapping evidence exists,[5] could be responsible for the observed course of the reaction.

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§ Rapid quenching of the acid solution of (I) with excess of methanol yields the expected methyl ether.

[1] For recent reviews see M. Cais in "Aromaticity, Pseudo-aromaticity, Anti-aromaticity", eds. E. D. Bergmann and B. Pullman, The Israel Academy of Science and Humanities, Jerusalem and Academic Press Inc., New York, 1971, pp. 96—113; M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 436.

[2] K.Schlogl and H. Egger, *Monatsh. Chem.*, 1963, **94**, 376, reported β-chlorovinylferrocene as an oil. Our compound had m.p. 46—48° and it exhibited the typical *trans* =CH i.r. absorption at 930 cm^{-1} as well as an AB quartet in the n.m.r. spectrum centred at δ 6·43 p.p.m. (downfield from Me_4Si), J_{AB} 14 Hz.

[3] Recently, W. Reeve, R. Brown, and T. F. Steckel, *J. Amer. Chem. Soc.*, 1971, **93**, 4607, reported the unexpected formation of gem-dichloroalkenes in reactions of Grignard reagents with tosylates of aryl-, alkyl-, and alkynyl-(trichloromethyl)methanols. A radical mechanism has been tentatively suggested for this reaction.

[4] A. Eisenstadt, D.Sc. Thesis, Technion-Israel Institute of Technology, July, 1967.

[5] P. Ashkenazi and M. Cais, manuscript in preparation.