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SOME ATTEMPTS TO PREPARE FERROCENYLACETONE

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SUMMARY

Attempts to make ferrocenylacetone by decomposition of ferrocenylmethyl diazomethyl ketone and Claisen condensation of ferrocenylacetonitrile with ethyl acetate are described. Products of both these reactions have been identified.

INTRODUCTION

There are not many reports on preparation of compounds containing a methylene group between the ferrocene ring and the carbonyl group. The preparation of ferrocenylacetaldehyde was described by Schlögl[1], and that of ferrocenylmethyl phenyl ketone by Pauson[2]. The synthesis of ferrocenylacetone by treatment of (chlormercuri)ferrocene with isopropenyl acetate under $PdCl_2$/LiCl catalysis was described very recently by Kasahara *et al.*[3].

We describe below two attempts to prepare ferrocenylacetone by methods which give good results in benzene chemistry.

RESULTS AND DISCUSSION

We first examined the preparation of ferrocenylmethyl diazomethyl ketone (I) and its transformation to ferrocenylacetone (II). Treatment of an ether solution of diazomethane with ferrocenylacetic acid chloride gave reasonable yields of diazomethyl ketone (I) when reactions were carried out at low temperatures in the absence of light. Reactions at room temperatures were unsuccessful. Ferrocenylmethyl diazomethyl ketone (I) is very stable in the solid state, but its solutions are extremely sensitive to light and heat.

Treatment of the ferrocenylmethyl diazomethyl ketone with hydriodic acid caused much decomposition. Solutions of the product are extremely sensitive to light, heat and air, and because of this purification by column chromatography was unsuccessful. A yellow oil was however, obtained by quick work-up of the reaction mixture, and gave good NMR, IR and mass spectra which confirmed the presence of ferrocenylacetone, (II). The yields were lower than 10%. The ferrocenylacetone, (II), was easily oxidized by air to ferrocenylpropanedione, (III), but much decomposition occurred.

Claisen condensation of ferrocenylacetonitrile with ethyl acetate appeared to proceed smoothly, but the product was not the expected nitrile of 2-ferrocenylacetoacetic acid. On the basis of the NMR, IR, and mass spectra we think that the product is ferrocenylacetylketeneimine, (IV). Attempts to carry out acid hydrolysis of (IV) were unsuccessful; the material was either extensively decomposed or recovered unchanged. By column chromatography on SiO_2, or on long standing (1 year) (IV) was converted into a new compound, which was judged to be the nitrile of 2-ferrocenylacetoacetic acid, (V), on the basis of its spectra.

Hydrolysis of ferrocenylacetylketeneimine under the conditions used in the preparation of phenylacetone[4,5] was not successful, both sulphuric and phosphoric acid causing extensive decomposition. However, some ferrocenylacetonitrile (20%) was isolated in the second case.

Column chromatography of (IV) on Al_2O_3 was unsatisfactory because a Thorpe condensation occurred to give 3,5-diferrocenyl-4-imino-5-cyano-2,6-heptanedione. Such condensation of ferrocenylacetonitrile was described by Pauson[6].

The behaviour of ferrocenylacetone resembles that of ferrocenylacetaldehyde, ferrocenylmethyl phenyl ketone[2], and ferrocenylacetonitrile, all of which are unstable in the solid state also. In all these cases there is a methylene group between the ferrocene ring and a strongly electron withdrawing group, and it seems likely that instability is associated with the ease of formation of the corresponding α-carbanions; such carbanion formation has been demonstrated, for example, by the smooth condensation of ferrocenylacetonitrile with *p*-chlorobenzaldehyde[7], by the formation of the dianion from ferrocenylacetonitrile[8], and the autocondensation of ferrocenylacetaldehyde[1].

EXPERIMENTAL

Melting points were determined with a Koffler block and are not corrected. The IR spectra were recorded on a Zeiss UR 20 spectrophotometer in the 700–3500 cm^{-1} range using NaCl optics. The wave number scale of the instrument was calibrated with the standard spectrum of polystyrene. The ^1H NMR spectra were measured on Perkin–Elmer 60 MHz and Tesla BS 487A 80 MHz instruments. Tetramethylsilane was used as internal standard.

Preparation of ferrocenylmethyl diazomethyl ketone, (I)

A solution 5.7 g (0.02 mol) of ferrocenylacetic acid chloride in diethyl ether (150 ml) was added dropwise to a solution of approximately 3 g of diazomethane in 400 ml of diethyl ether at such a rate that the temperature of the mixture did not rise above 5°. The mixture was set aside at 0°–3° for 72 h, and was then concentrated to 150 ml and filtered. Crystallization gave 3 g (50.3%) of ferrocenylmethyl diazomethyl ketone as orange crystals, m.p. 105–107°, after repeated crystallization from diethyl ether. (Found: Fe, 21.10; N, 10.58. $C_{13}H_{12}FeN_2O$ calcd.: Fe, 20.75; N, 10.40%.) Mass spectrum (*m/e*): $(C_{13}H_{12}FeN_2O)^{+\cdot}$ 268.02986 $\rightarrow (C_{13}H_{12}FeO)^{+\cdot}$ 240.02371 $\rightarrow (C_{12}H_{12}Fe)^{+}$ 199.02097. NMR (60 MHz, CS_2, τ): 5.02(s, 1H); 6.00(s, 9H); 6.80 (s, 2H). IR (Nujol, cm^{-1}): 1005 m, 1105 m, 1635 s, 2100 s. (The characteristic vibrations are given in this and all other cases.)

Preparation of ferrocenylacetone (II)

Azeotropic hydriodic acid (4 ml) was slowly added to a solution 0.4 g (0.0015 mol) of ferrocenylmethyl diazomethyl ketone in 40 ml of CCl_4 contained in a separating funnel. The mixture was carefully shaken, and N_2 was evolved and heat liberated. After evolution of N_2 had ceased, the mixture was washed with water, 10% aqueous $Na_2S_2O_3$, and then water again. After a short drying over anhyd. Na_2SO_4 the solution was filtered, and the CCl_4 was evaporated from the filtrate under a slow stream of nitrogen. The residual yellow oil (less than 10%) was dissolved in CCl_4, and spectra were recorded with this solution. Mass spectrum (*m/e*): $(C_{13}H_{14}FeO)^{+\cdot}$ 242 → $(C_{11}H_{11}Fe)^{+}$ 199 → $(C_5H_5Fe)^{+}$ 121. NMR (80 MHz, CCl_4, τ): 6.05(s, 9H); 6.84(s, 2H); 8.05(s, 3H). IR (CCl_4, cm^{-1}): 1005 m, 1109 m, 1720 s.

Oxidation of ferrocenylacetone; the preparation of ferrocenylpropanedione, (III)

A solution of ferrocenylacetone in CCl_4 or benzene was allowed to stand in a closed flask for several hours, during which time the colour of the solution changed from yellow to red-violet, and some brown powder was precipitated. Similar behaviour was observed when air was bubbled through the solution. The organic material was extracted into benzene and the solution was chromatographed on SiO_2 (Kavalier, Votice). Benzene eluted first a small amount of ferrocenylacetone (the colour was changed by evaporation of benzene), and then a red-violet band which afforded violet material after evaporation of the benzene. Crystallization from petrol gave violet crystals of ferrocenylpropanedione (III) m.p. 100–102°. (Found: C, 61.84; H, 4.35; Fe, 21.53. $C_{13}H_{12}FeO_2$ calcd.: C, 61.23; H, 4.71; Fe, 21.77%.) Mass spectrum (*m/e*): $(C_{13}H_{12}FeO_2)^{+\cdot}$ 256.0205 → $(C_{10}H_9)^{+}$ 129.0700. NMR (60 MHz, CCl_4, τ): 5.06 (t, 2H); 5.48(t, 2H); 5.87(s, 5H); 7.62(s, 3H). IR (CS_2, cm^{-1}): 1000 m, 1105 m, 1646 s, 1712 m.

A third, violet, band was observed, but there was not sufficient material for characterization.

Preparation of ferrocenylacetylketeneimine, (IV)

To a stirred solution 3.2 g (0.0025 mol) of napthalene in 10 ml of THF was added 0.57 g (0.0025 g-atom) of sodium. The temperature rose from 18 to 30°, and the colour changed to deep green. The mixture was stirred until all sodium was dissolved (2.5 h), then cooled to −10°, and 4.5 g (0.02 mol) of ferrocenylacetonitrile and 2.6 g (0.03 mol) of ethyl acetate (dried over P_2O_5) were added at a rate such that the temperature of the mixture did not rise above 15°. The mixture was subsequently stirred and heated for 2 h to 60° (internal temperature).

The precipitate was filtered off with suction, washed with ether, and then dissolved in 100 ml of water. The solution was filtered, cooled with ice, and then treated with 7 ml of acetic acid. The yellow-brown solid was separated and dried. 2.7 g (51%) of material was isolated, and after crystallization from a benzene/petrol 1/1 mixture gave brown-red crystals of ferrocenylacetylketeneimine (IV), m.p. 121–122°. (Found: Fe, 20.90; N, 5.08. $C_{14}H_{13}FeNO$ calcd.: Fe, 20.92; N, 5.23%.) Mass spectrum (*m/e*): $(C_{14}H_{13}FeNO)^{+\cdot}$ 266 → $(C_{12}H_{10}FeN)^{+}$ 224. IR (Nujol, cm^{-1}): 1005 m, 1106 m, 1665 s, 2214 s. NMR (80 MHz, $CDCl_3$, τ): 5.81 (m); 7.29(s); 7.86(s). (Integration is not good enough owing to the poor solubility.)

Ferrocenylacetylketeneimine was changed by chromatography on SiO_2 (with benzene as eluant) to (V), the brown-yellow nitrile of 2-ferrocenylacetoacetic acid, m.p. 185° (from benzene/petrol). The same material was produced when (IV) was allowed to stand for 1 year. (Found: Fe, 20.73; N, 5.10. $C_{14}H_{13}FeNO$ calcd.: Fe, 20.92; N, 5.23%.) Mass spectrum (*m/e*): $(C_{14}H_{13}FeNO)^{\dot{+}}$ 267.0351 → $(C_{12}H_{10}FeN)^{\dot{+}}$ 224.0149. IR (Nujol, cm^{-1}): 1007 m, 1110 m, 1729 s, 2246 w. The substance was not sufficiently soluble to give a good NMR spectrum.

Chromatography of ferrocenylacetylketeneimine on Al_2O_3 (Brockman II, Reanal Budapest), with benzene as eluant gave yellow crystals; crystallisation from benzene gave material of m.p. 275° (decomposition), which was identified as 3,5-diferocenyl-4-imino-5-cyano-2,6-heptanedione. (Found: Fe, 21.49; N, 5.17. $C_{28}H_{26}Fe_2N_2O_2$ calcd.: Fe, 20.92; N, 5.23%.) Mass spectrum (*m/e*): $(C_{28}H_{24}Fe_2N_2O_2)^{\dot{+}}$ 532.0533 → $(C_{27}H_{23}Fe_2NO)^{\dot{+}}$ 490.0509. IR (Nujol, cm^{-1}): 1003 m, 1109 m, 1636 m, 1692 s, 1716 s, 2257 w, 3400 m. The poor solubility prevented the recording of a satisfactory NMR spectrum.

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