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Ferrocenylanthracene polymers: the direct synthesis using "Lawesson's Reagent"

Ian R. Butler [*], Alfonso G. Caballero, Glenn A. Kelly

Department of Chemistry, University of Wales, Bangor, Bangor, Gwynedd LL57 2UW, UK

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Abstract

A method for polymerizing ferrocenylanthraquinone compounds was investigated, using a methodology developed originally for the polymerization of 9,10-anthracenedithiols. This procedure uses an in situ reaction of "Lawesson's Reagent" (*p*-methoxyphenylthionophosphine sulphide dimer), with anthraquinone allowing polymerization to proceed across the 9- and 10-positions of the ferrocenylanthraquinones resulting in polymers with pendant ferrocene groups on the polymer backbone. Monomers used for these reactions were anthraquinone (literature comparison), 2-ferrocenylanthraquinone and 2,6-diferrocenylanthraquinone.

Keywords: Anthraquinone; Ferrocene; Ferrocenylanthraquinone; "Lawesson's Reagent"; Polymers

1. Introduction

Polymers with ferrocene side groups are of significant interest as potential electrode mediators and as materials for the inclusion into electronic devices [1–3]. The use of anthracene as a backbone would provide an excellent conjugated polymer with well-defined rigid structures [4]. Materials containing anthracene are of particular interest because of their potential electroluminescent properties [5]. This work is a continuation of our longstanding interest in the area of ferrocenylanthracene chemistry [6]. The starting materials for the polymerization experiments were anthraquinone, 2-ferrocenylanthraquinone and 2,6-diferrocenylanthraquinone. The synthesis of 1-ferrocenylanthraquinone was first reported by Roberts [7] in 1990 from the reaction of the commercially available 1-diazoniumanthraquinone (Aldrich Fast Red AL Salt) and ferrocene. A one-pot synthesis of a mixture of 2-ferrocenylanthraquinone and 2,6-diferrocenylanthraquinone has recently been reported by Coudret and Launay [8], but these compounds were not isolated or characterized. In this paper we report the synthesis and characterization of these two compounds prior to their polymerization with "Lawesson's Reagent" or *p*-methoxyphenylthionophosphine sulphide dimer (see Fig. 1).

This reagent is well known to polymerize diketones such as anthraquinone [9], as it an oxygen scavenger replacing the oxygen with sulphur. It is a convenient thiation reagent for ketones, amides, esters and *S*-substituted thioesters [10]. In the case of anthraquinone it is long-established that the thioketone is unstable and thus forms a polymer with persulphide bridges. This polymer, anthracene polydisulphide, has also been reported to undergo reduction with sodium borohydride to give anthracene 9,10-dithiol which has in turn been used as a monomer in the reaction with 9,10-diethynylanthracene to give conjugated acetylene polymers with anthracene backbones [11].

2. Experimental

2.1. Preparation of 2-ferrocenylanthraquinone, method 1

Using a standard literature procedure [10], concentrated HCl (7 ml) was added to 2-aminoanthraquinone (2.73 g, 0.0125 mol) at 30 °C. Then a solution of sodium

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[*] Corresponding author. Tel.: +44-0-12-48-382-390; fax: +44-0-12-48-370-528.

E-mail address: chs026@bangor.ac.uk (I.R. Butler).

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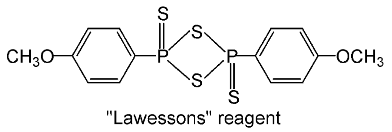


Fig. 1.

nitrite (0.87 g, 0.0125 mol) in distilled water (5 ml) was added dropwise while stirring. The temperature was then raised to 50 °C. A solution of warm distilled water (80 ml) was then added and the mixture was filtered while hot. The unreacted solid was washed with warm distilled water. To the warm filtrate, NaCl (24 g) was added and the mixture was stirred for 10 min and then left to cool. The yellow precipitate was then filtered, washed with saturated NaCl solution and dried in air. Yield: 1.40 g. The yellow product was used directly in the next step without characterization.

To the previously formed 2-anthraquinone diazonium chloride (1.40 g, 0.0052 mol) in dry CH_2Cl_2 (50 ml), ferrocene (2.90 g, 0.015 mol) in dry CH_2Cl_2 (50 ml) was added dropwise while stirring. The mixture was then stirred overnight at room temperature. The mixture was then filtered, the filtrate concentrated under vacuum and suspended in toluene. The suspension was loaded onto a column of silica gel and the product eluted with petrol (40/60 °C) and diethyl ether (1:1).

Yield 0.44 g (22%). Appearance – blue/black crystals, mp 174 °C (uncorr.) δ_H ($CDCl_3$): 4.04(s, 5H), 4.46(t, $J = 1.8$ Hz, 2H), 4.82(t, $J = 1.8$ Hz, 2H), 7.79(m, 3H), 8.19(d, $J = 8$ Hz, 1H), 8.30(m, 3H). δ_C(62.9 MHz, $CDCl_3$): 67.23(2C, cyclopentadienyl β), 70.20(5C, cyclopentadienyl, unsubstituted), 70.58(2C, cyclopentadienyl α), 82.12(C, cyclopentadienyl ipso), 123.70, 127.17, 127.20, 127.63, 130.78, 133.50, 133.56, 133.61, 133.81, 134.12, 147.58, 156.33, 182.75(CO), 183.5(CO). MS (EI) m/e (rel. int.): 392 M^+. (100%), 213(15%), 196(12%), 121(32%). Elemental analysis ($FeC_{24}H_{16}O_2$); calc. %: C 73.47, H 4.08, found %: C 73.79, H 4.05. This compound has been also characterized by single crystal X-ray diffraction, the results of which will be presented in a general synthetic manuscript with the crystallographic structures of a range of ferrocenyl anthraquinones.

2.2. Preparation of 2-ferrocenylanthraquinone, method 2

2-Aminoanthraquinone (60 g, 0.269 mol, 1 equiv.) was dissolved in 100 ml of concentrated sulphuric acid under nitrogen atmosphere. To the well stirred solution, nitrosyl sulphuric acid (37.57 g, 0.300 mol, 1.1 equiv.) was added slowly and the mixture was allowed to react for 15 min. Afterwards, the reaction mixture was slowly added to an ice/water bath. The precipitate was filtered, washed with 200 ml of water and air dried as the diazonium sulphate salt. Excess of ferrocene (35 g, 0.188 mol) was dissolved under nitrogen atmosphere in 200 ml of dichloromethane in another flask. To this ferrocene solution was added the dried diazonium salt and the mixture was stirred for 2 h. The product formation was followed by TLC; the product appears as a violet spot. The final solution was evaporated and the residue was columned on a chromatographic silica gel column. The final product was eluted with 100% ether as a violet powder. Yield 43.7 g (36%).

2.3. Preparation of 2-ferrocenylanthraquinone, method 3

1-Ferroceneboronic acid (0.25 g, 1.0×10^{-3} mol) and 2-bromoanthraquinone (0.35 g, 1.2×10^{-3} mol) were dissolved in a solution of dry DMF (30 ml) and potassium carbonate (0.20 g). Tetrakis(triphenylphosphine) palladium (0) (0.05 mol%) was then added under N_2 gas. The mixture was then heated to reflux for 20 min under N_2 gas (after 2 min the solution changed from dark orange to violet). After cooling to room temperature, the mixture was stirred for two days. The product was purified by column chromatography using neutral alumina and diethyl ether and petroleum ether (40/60 °C) as eluting solvent. The product was found to be identical to 1-ferrocenyl-2-anthraquinone. Yield 0.39 g (91%) δ_H (250 MHz, $CDCl_3$): 4.06(s, 5CH), 4.48(s, 2CH), 4.84(s, 2CH), 7.39–8.42(m, 7ArH).

2.4. Preparation of 2,6-diferrocenylanthraquinone

To a solution of nitrosyl sulphuric acid (2.5 g) in sulphuric acid (15 ml, 78%), 2,6-diaminoanthraquinone (1.18 g, 0.005 mol) was added with vigorous stirring. After stirring for 2 h, the mixture was filtered and fluoroboric acid (25 ml, 50%) was then added to the filtrate. A white precipitate was then formed which was isolated by filtration, washed with water and dried in air. The 2,6-anthraquinone tetrazonium boron tetrafluoride salt was then used directly in the next step without characterization.

To the crude 2,6-anthraquinone tetrazonium salt in dichloromethane (50 ml), ferrocene was added (2.5 g, 0.01 mol) while stirring. The mixture was then stirred overnight at room temperature. The mixture was then filtered, the solvents were evaporated under vacuum and the product was purified by flash chromatography (solvents: 20% diethyl ether/dichloromethane). Yield 0.60 g (21%). Appearance blue/black solid. δ_H (250 MHz, $CDCl_3$): 4.09(s, 10CH), 4.51(s, 4CH), 4.88(s, 4CH), 7.85(m, 2ArH), 8.30(m, 4ArH). MS (EI) m/e (rel. int.): 576 M^+ (30%), 392 (100%), 379 (55%), 363 (18%), 215 (20%).

Accurate mass: calc. 576.047507, found 576.049562. Elemental anal.: calcd; C, 70.83%, H, 4.16, found 67.94%, 4.25.

2.5. Formation of polymers from 2,6-diferrocenylanthraquinone

To a stirred solution of "Lawesson's Reagent" (0.30 g, 7×10^{-4} mol) in boiling chlorobenzene (30 ml), 2,6-diferrocenylanthraquinone (0.20 g, 3×10^{-4}) was added in hot chlorobenzene (50 ml). The mixture was then heated to reflux for 1.5 h. The mixture was then allowed to cool and the brown solid was filtered. Yield 125 mg (67%). Petroleum ether(40/60 °C) was added to the mother liquor to give a further crop of brown crystals. Yield 25 mg (14%). Overall yield – 81%.

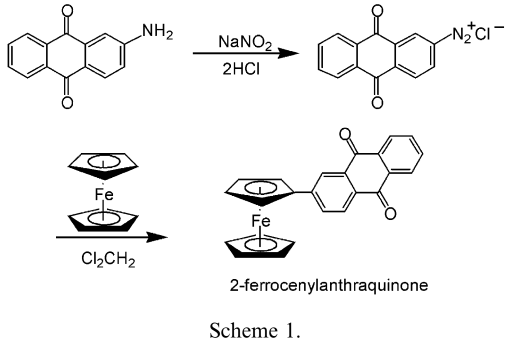
δ_H(250 MHz, $CDCl_3$): 4.03(br. s, 10CH), 4.36(br. s, 4CH), 4.78(br. s, 4CH), 7.69(br. s, 3ArH), 8.31(br. s, 3ArH).

A similar reaction of 2-ferrocenylanthraquinone under identical experimental conditions gave a deep green/black polymer which was characterized by solid state NMR as follows. ^{13}C (125.77 MHz) δ: 33.38, 56.26, 73.30 with underlying ca. 70.00–82.00, broad resonances, 90.2, 118.31, 133.23, 163.29, 174.63, 204.61. The deep red polymer which was prepared from Lawesson's Reagent and unsubstituted anthraquinone using the literature methodology was similarly characterized ^{13}C (125.77 MHz) δ: (43.14, 51.43, 85.62, 127.56, 134.42, 169.30, 176.14, 210.57, 217.36, 252.76).

3. Results and discussion

The ferrocenylanthraquinone monomer compounds were all synthesized from cheap and commercially available aminoanthraquinone starting materials. Several procedures were initially used to form the precursor, 2-ferrocenylanthraquinone, beginning with diazotization of 2-aminoanthraquinone using a mixture of sodium nitrite and hydrochloric acid [12]. The diazonium chloride salt was then reacted with an excess of ferrocene in dichloromethane, giving a dark blue solid in 22% yield (see Scheme 1).

The poor yields prompted the use of an alternative diazotization procedure using nitrosyl sulphuric acid as the active reagent. Thus diazotization with nitrosyl sulphuric acid, using standard conditions [13], followed by reaction with ferrocene gave the product in 36% yield. Again although the reaction yields are significantly better the reaction workup and product isolation procedure was tedious. An improved procedure involved the catalytic "Suzuki" coupling reaction of 1-ferroceneboronic acid [14] and 2-bromoanthraquinone (from the "Sandmeyer" reaction of 2-diazoniumanthraquinone and copper(II) bromide) using tetrakis(triphenylphosphine) palladium (0) as catalyst using standard conditions [15], giving the product in 91% yield (see Scheme 2).

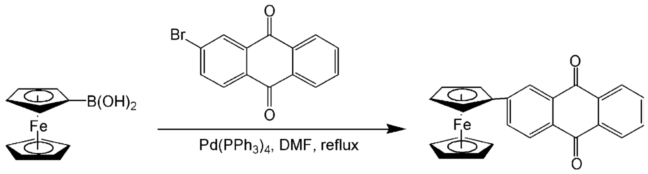


Scheme 1.

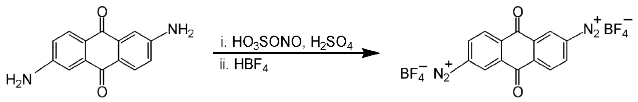
An attempt was first made to synthesize 2,6-diferrocenylanthraquinone from the tetrazonium chloride salt, but the yield from this procedure was very low (1%) due to the relative instability of this particular salt. Therefore our starting materials were finally synthesized by converting the tetrazonium chloride salt of the anthraquinone into tetrazonium tetrafluoroborate [13]. 2,6-Diaminoanthraquinone is first reacted with nitrosyl sulphuric acid in concentrated sulphuric acid to create the tetrazonium salt with bisulphate as the counter ion. The mixture is then reacted immediately with tetrafluoroboric acid to give the more stable tetrazonium tetrafluoroboric salt (see Scheme 3).

This more stable salt was then reacted with an excess of ferrocene in dichloromethane to give 2,6-diferrocenylanthraquinone in improved yields (21%) (see Scheme 4).

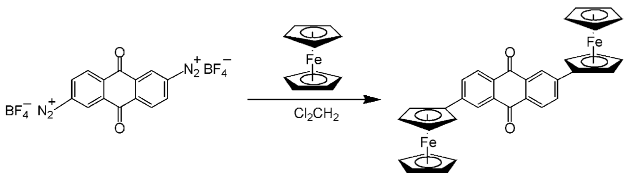
This dark blue black solid was characterized by NMR and mass spectrometry and exhibited a clean



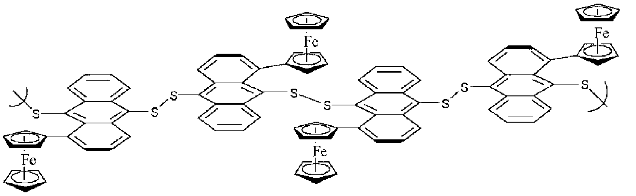
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

parent ion at *m*/*e* 576. The main by-product of the reaction was 2-ferrocenylanthraquinone. The NMR spectra were as anticipated with the ferrocenyl resonances observed at 4.09δ (unsubstituted rings), 4.51δ and 4.88δ.

3.1. Polymerization of 2,6-diferrocenylanthraquinone and 2-ferrocenylanthraquinone

Once the 2,6-diferrocenylanthraquinone and 2-ferrocenylanthraquinones had been isolated, the next experiments carried out were to see if the carbonyl groups on the 9- and 10-positions on the anthraquinone could be polymerized forming a polymer with pendant ferrocenyl units. When these diferrocenyl compound was added to a hot solution of "Lawesson's Reagent" [16] (two equivalents) in chlorobenzene in each case a green/black to dark brown polymer material resulted after the mixtures were heated to reflux for 1.5 h (see Scheme 5).

The products were isolated as solids which slowly precipitated from the solution on cooling in 45% (monoferrocenyl) and 81% (diferrocenyl) yield. More soluble oligomeric fractions of these polymers were characterized by ^{1}H NMR in deuterated chloroform. The spectra in each case exhibited very broad resonances, typical of polymeric material, in the region of between δ4.03 and 4.78 ppm indicating the presence of the cyclopentadienyl protons. Broad resonances in the region of δ7.69 and 8.31 ppm again were a characteristic of the aromatic environments of the anthracenyl protons.

Similar polymerization reactions were carried out using anthraquinone (run as a comparison according to the literature methodology), and then a 1:1 mixture of anthraquinone and 2-ferrocenylanthraquinone were also produced. These were characterized using solid state NMR. The elemental analytical data obtained was unsatisfactory and it became evident that some Lawesson's Reagent was entrained in these polymers even after washing, since ^{13}C NMR resonances were observed at ca. 33 and 56 ppm. This was consistent with the results obtained of a control polymer prepared from only anthraquinone and Lawesson's Reagent which showed similar resonances at ca. 43 and 51 ppm.

4. Conclusions

The synthesis of ferrocene containing polysulphide polymers of anthracene have been obtained for the first time. These materials will now be used as precursors for material science applications.

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References

[1] M.R. Buchmeiser, Macromolecules 30 (1997) 2274.
[2] P.D. Hale, T. Inagaki, H.I. Karan, Y. Okamoto, T.A. Skotheim, J. Am. Chem. Soc. 111 (9) (1989) 3482.
[3] G.P. Kittleson, H.S. White, M.S. Wrighton, J. Am. Chem. Soc. 107 (1985) 7373.
[4] R. Gooding, C.P. Lillya, C.W. Chien, J. Chem. Soc. Chem. Commun. (1983) 151.
[5] G. Wagner, R. Herrmann, W. Scherer, J. Organomet. Chem. 516 (1996) 225.
[6] I.R. Butler, L.J. Hobson, S.J. Coles, M.B. Hursthouse, K.M. Abdul Malik, J. Organomet. Chem. 540 (1997) 27.
[7] R.M.G. Roberts, J. Organomet. Chem. 388 (1990) 181.
[8] V. Gonzalo, C. Coudret, C. Patoux, J.-P. Launay, C.R. Acad. Sci. Paris 2 (IIc) (1999) 321.
[9] M.V. Lakshmikantham, M. Levinson, M. Menachery, M.P. Cava, J. Org. Chem. 51 (1986) 411.
[10] M.P. Cava, M.I. Levinson, Tetrahedron 41 (1985) 5061.
[11] E. Kobayashi, J. Jiang, H. Ohta, J. Furukawa, J. Polym. Sci., Polym. Chem. Ed. 28 (1990) 2641.
[12] S.R. Sandler, W. Karo, Organic Functional Group Preparations 12(I) (1968).
[13] K.-Y. Lee, I.W. Tarnawskyi, S. Kaplan, Can. J. Chem. 69 (1991) 1183.
[14] H. Schechter, J.F. Helling, J. Org. Chem. 26 (1961) 1034.
[15] C. Imrie, C. Loubser, P. Engelbrecht, C.W. McLeland, J. Chem. Soc., Perkin Trans. 1 (1999) 2513.
[16] (a) S. Scheibye, J. Kristensen, S.O. Lawesson, Tetrahedron 35 (1979) 1339;
(b) B.S. Pedersen, S.O. Lawesson, Tetrahedron 35 (1979) 2433.