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METALLOCENE POLYMERS

XXVI. ISOMERIC TERFERROCENYLS IN THE POLYRECOMBINATION REACTION OF FERROCENE*

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SUMMARY

A re-examination of the oligonuclear by-products arising in the previously reported polyrecombination reaction of ferrocene in the presence of tert-butyl peroxide has revealed the presence of an additional trinuclear compound, m.p. 198–200°, to which the structure of 1,2-diferrocenylferrocene (1,2-terferrocenyl) is ascribed on the basis of spectroscopic and other evidence. The compound is found to be identical with an authentic sample synthesised by other workers. Separation from other oligonuclear ferrocenes is accomplished by column chromatography. This result, coupled with the firm identification of the remaining two possible terferrocenyl isomers of the previous study as 1,3-terferrocenyl and 1,1′-terferrocenyl, necessitates a reassignment of the compound, m.p. 260–265°, which had tentatively been identified in that study as a terferrocenyl.

INTRODUCTION

Ever since our reinvestigation of the polyrecombination reaction of ferrocene[1,2], in which three compounds believed to be terferrocenyls had been isolated from the reaction products, the question of their proper structural assignment has puzzled us. The only isomer unambiguously identified at that time was the terferrocenyl of m.p. 196–197°, which proved to be identical (X-ray diffraction pattern; mixture m.p.) with authentic (II) (1,3-diferrocenylferrocene) prepared by an independent synthetic route[3].

No definite structures were ascribed in that work[1,2] to the remaining two species isolated, one melting at 226–228° and the other at the broad range 260–265°. Hata and coworkers[4,5] previously prepared a terferrocenyl with m.p. 226.5–227.2°, which they were able to identify as the heteroannularly arranged 1,1′-diferrocenylferrocene, (III). A comparison by spectroscopic data (IR, ^{1}H NMR, and X-ray diffraction) of our compound melting at 226–228° with Hata's product has since

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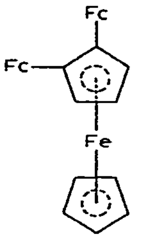
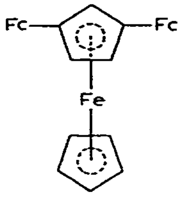


(I)



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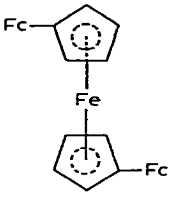

(III)

shown[6] the two products to be identical. [For other preparations of (III) see Rinehart *et al.*[7] (m.p. 215–234°) and, more recently, Rausch *et al.*[8] (m.p. 224–226°).] The assignment of (III) for compound m.p. 226–228° finds corroboration in the identity of the IR spectrum with that published by Nesmeyanov and coworkers[9] for a terferrocenyl melting at 212.5–214.5°, for which, on the basis of an X-ray diffraction study[10], there can be no doubt as to its heteroannularity*.

The identification of two of the terferrocenyls as the 1,3- and 1,1'-isomers, (II) and (III), would suggest structure (I), 1,2-diferrocenylferrocene, as the only assignment remaining for the third compound (m.p. 260–265°) of our previous study. However, some doubt as to such assignment arose immediately[1] on the basis of the electronic absorption spectrum. The compound, if indeed the 1,2-isomer, should for steric reasons lack the coplanarity visualized for (II) or (III). One should, hence, expect bathochromic shifts of the absorption maxima in going from the 1,2- to the 1,3- and 1,1'-isomers. Experimental results show the opposite (Table 1), the compound invariably exhibiting higher wavelengths and extinction coefficients for the bands listed. This inconsistency, coupled with the recent report of the synthesis of (I) (m.p. 191–193°) by Goldberg and Breland[14] and, independently (m.p. 202–204°), by Rausch's group[13], has prompted us to re-examine our earlier[1,2] results in hopes of finding a compound melting in the 200° range that we might have overlooked in the original work.

RESULTS AND DISCUSSION

In a typical polyrecombination reaction of the type described in the earlier work[1,2], ferrocene was allowed to react with excess tert-butyl peroxide at 200°, the peroxide addition being extended over a period of 10 h. From the low-molecular weight portions of the crude polyrecombination product, repeated column chromatography furnished in 0.12% yield a trinuclear compound, m.p. 198–200°, in addition to the previously[1,2] isolated terferrocenyls (II) and (III) and the substance with m.p. 260–265°. The compound ranks in adsorbability between the last-named substance (eluted first) and terferrocenyl (III) (eluted subsequently); as the various zones showed some overlapping even in most careful experimental work, it doubtlessly remained

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* The discrepancies in melting point ranges found for (III) and, somewhat less so, for (I) and (II) appear to be a common feature of other oligonuclear ferrocenes described in the literature and perhaps must be traced to the extraordinary difficulties encountered in their purification. We have also noticed the melting temperatures of such compounds to be highly sensitive to the conditions of test.

buried in the trailings of (III) in the previous work and so escaped detection.

The assignment of this compound to the expected 1,2-terferrocenyl structure (I) follows from analytical and spectroscopic evidence. Elemental analysis and molecular weight determinations by vapor-pressure osmometry are in accord with a terferrocenyl composition. The electronic absorption spectrum, in accord with expected behaviour for (I), shows maxima that are hypo- and hypsochromically shifted relative to (II) and (III) and practically coincide in position with those of biferrocenyl (Table 1). The infrared spectrum, similar to that of biferrocenyl, exhibits the 1000 and 1110 cm^{-1} bands[16] (the latter as doublet, with stronger peak at lower frequency) and the 1410 cm^{-1} absorption* all in distinctly higher intensity (relative to the 480 cm^{-1} metal–ring stretching peak) than does the spectrum of (III), in agreement with a homoannular structure of the center unit. (Quantitative homoannularity[23] measurements are not feasible with tri- and polynuclear ferrocenes owing to interference by other absorptions in the critical regions[5].) The substitution band at 1025 cm^{-1} (probably an a_1 fundamental, C–H in-plane deformation mode) appears in moderate-

TABLE 1

ELECTRONIC ABSORPTION MAXIMA

Compound	*M.p.* (°C)	λ_{max}[a] (*nm*)		
Biferrocenyl	237–239[b] 238–240[c] 227.5–229.0[d]	295 (8470)	345 (sh) (950)	450 (600)
1,2-Terferrocenyl (I)	198–200[b] 202–204[e] 191–193[f]	295 (9050)	345 (sh) (1660)	449 (780)
1,3-Terferrocenyl (II)	206–208[b,g] 196–197[h]	301 (12500)	349 (sh) (2200)	455 (1120)
1,1′-Terferrocenyl (III)	228–229[i] 226–228[h] 224–226[c] 212.5–214.5[j] 226.5–227.2[k] 215–234[l]	302 (15700)	350 (sh) (2500)	454 (1290)
Compound m.p. 260–265°	260 –265[h]	313 (22600)	362 (sh) (3800)	456 (1910)

[a] In abs. ethanol. Molar extinction coefficient in parentheses. [b] Our work. [c] Ref. 8. [d] Refs. 11, 12. [e] Ref. 13. [f] Ref. 14. [g] Ref. 3; taken in vacuum-sealed capillary (197–198° in open capillary). [h] Ref. 2. [i] Ref. 6. [j] Ref. 9. [k] Refs. 4, 5. [l] Ref. 7.

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* Arising from *sym.* and *asym.* ring C–C stretching vibrations and admixed strong in-plane bending and weak in-plane ring-deformation modes[17–20], this absorption frequently, but not invariably, shifts to shorter wavelengths on substitution of a cyclopentadienyl ring, becoming an a_1 mode in local C_{2v} symmetry (with a corresponding b_1 band near 1370 cm^{-1}). Attenuation of the 1410 cm^{-1} band thus may, in conjunction with the (more indicative) "9,10-μm rule" of Rosenblum[16], serve to indicate the presence of one or more substituted rings in a ferrocene compound[21]. For an obvious exception, see Willis *et al.*[22].

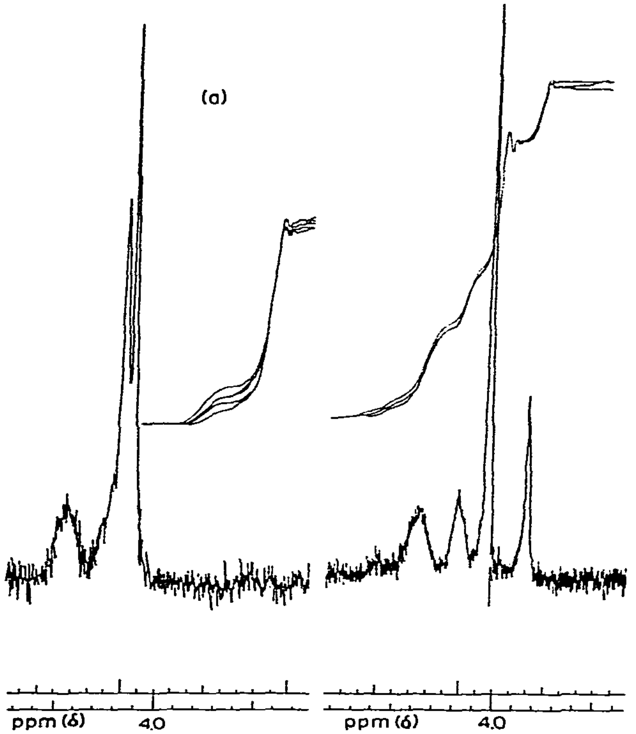

Fig. 1. ^{1}H NMR spectra ($CDCl_3$, 60 MHz): a: 1,2-terferrocenyl (I); b: 1,3-terferrocenyl (II).

ly high intensity. The 1050 cm^{-1} C–H out-of-plane deformation band, extremely weak in ferrocene, is shown here in enhanced intensity*. In addition, weak absorption appears at 1140 and 1242 cm^{-1} not shown by either (II) or (III). In the mass spectrum, the highly stable parent ion produces the basis peak (for ^{56}Fe) at *m/e* 554 (intensity 100) and the $[M+1]^+$ shoulder, *m/e* 555, in the intensity (40) expected for a trinuclear compound. The corresponding doubly charged species are found at 277(13) and 277.5(5.4), again in the proper intensity ratio. Loss of a cyclopentadienyl ring yields *m/e* 489(6), with metastable peak at 431.6. As in biferrocenyl[15], the CpFe ion, *m/e* 121, is highly abundant (19). A biferrocenyl ion, *m/e* 369, is created by loss of one ferrocenyl group. This homoannular ion cannot "back–bite" without preceding hydrogen transfer and, hence, remains highly abundant (16). [In contrast, the same process of ferrocenyl elimination in (III) produces the corresponding heteroannular ion, which readily substitutes the adjacent nucleus to form the very stable [0,0]-ferrocenophane ion. Hence we find the base peak in (III) at *m/e* 368**.] Final structural proof is derived from the identity of the ^{1}H NMR spectrum [Fig. 1a: spectrum of (II) is given in Fig. 1b for comparison] with that of Rausch's[13] compound (I) melting at

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* This band, due to IR-forbidden E_2 modes (ω_{25}, ω_{31}) in the C_{5v} symmetry of ferrocene[17,18], assumes the irreducible representation a_2 in the local C_{2v} symmetry of the substituted rings in biferrocenyl and III. In II, IR forbiddenness may be partially removed owing to relaxation of selection rules in the disubstituted center ring.

** It should be emphasised that the mass spectra here discussed were obtained at 250° inlet temperature. Different intensities may result from recordings at lower temperatures.

202–204°, for which the 1,2-disposition was ascertained through unambiguous synthesis*.

With the assignments of the three isomeric terferrocenyls (I)–(III) thus secured, there remains the problem of the structural identity of the compound, m.p. 260–265°, isolated and tentatively identified as a terferrocenyl in our earlier study[1,2]. A structural reassignment of this compound must await further experimental work.

EXPERIMENTAL

Instrumental analyses

All melting points are uncorrected and were taken in sealed, evacuated capillaries. Number-average molecular weights were determined in benzene solution on a Mechrolab Model 301 A vapour pressure osmometer. Infrared spectra (KBr pellets) were recorded on a Perkin–Elmer Model 521 spectrometer. Mass spectra (70 eV; 250° inlet temp.) were taken on a Varian–Mat CH5 mass spectrometer. High resolution ^{1}H NMR spectra, in $CDCl_3$ solution, were recorded at 60 MHz on Varian A-60 NMR spectrometer; chemical shifts, δ, in ppm relative to TMS.

Polyrecombination of ferrocene

Ferrocene (100.0 g, 0.538 mol), purified by recrystallisation from hexane, was treated at 200° under N_2 with reagent-grade tert-butyl peroxide (180.0 g, 1.231 mol) in the equipment, and by the procedure, described previously [1,2]. The overall peroxide addition time was 10 h. The cooled and solidified, semicrystalline product, 85 g, was extracted with hexane in a Soxhlet extractor, and the remaining hexane-insolubles, 26 g, were treated with boiling benzene to dissolve oligomeric and polymeric ingredients. The benzene solution, filtered from some insoluble matter and concentrated to 200 ml, was stirred into 800 ml of isopropanol to give a brown polymeric precipitate, which was filtered off, washed with the same precipitant, and dried for 5 days at 50° *in vacuo*. There was thus obtained 24.1 g of polymer, $\overline{M}_n$ 5800. The mother-liquors and isopropanol washings, combined with the hexane Soxhlet extract, were evaporated to dryness in a rotating evaporator, and the residue, taken up in hexane, was chromatographed under light protection on 3 kg of Merck alumina, activity grade (II), with hexane as the eluant. Following the elution of ferrocene (37.5 g) and biferrocenyl (3.9 g) as described[2], a broad third band emerged, which was subjected to a second chromatographic treatment in hexane solution on alumina of activity grade I. Subsequent to a very faint and neglected band probably containing traces of biferrocenyl, there was eluted an orange zone (band I), closely followed by a broad yellow (band II) and two narrow-spaced yellow zones (bands III and IV); a striated top zone, slow-moving and probably containing higher-molecular oligomers, was left on the column without further examination. The eluted fractions, after solvent stripping, were worked up as follows:

Band I. This fraction, after extraction with methanol for removal of admixed ferrocenyl tert-butyl ether[2], constituted 0.07 g of difficultly soluble, orange crystals

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* The compound, m.p. 191–193°, described by Goldberg and Breland[14] is not quite pure and, thus less suitable for comparative identification. Aliphatic constituents, as indicated by the authors, are manifested in the IR (C–H stretching at 2860–2960 cm^{-1}, C–H bending at 1440 cm^{-1}). In addition to a sharp singlet near δ 3.8 ppm superimposed on spectrum of pure (I) [admixture of (II)?, *cf.* Fig. 1], the ^{1}H NMR spectrum shows an unaccountable broad absorption near 4.2 ppm.

melting over the broad range 255–270° and giving an IR spectrum essentially identical with that of compound m.p. 260–265° of the previous study[1,2]. The product was set aside for future structural elucidation.

Band II. The amber-coloured, partly oily residue was recrystallised from heptane to give 0.12 g (0.12%) of crude (I), m.p. 193–196° (sintering at 185°), soluble in hydro- and halocarbons, and readily sublimable *in vacuo* at 100°. After several more recrystallisations, the terferrocenyl was obtained as orange needles, m.p. 198–200°. (Found: C, 65.20; H, 4.90; Fe, 30,34; mol. wt., 566. $C_{30}H_{26}Fe_3$ calcd.: C, 65.03; H, 4.73; Fe, 30.24%; mol. wt., 554.)

Bands III and IV. Crude terferrocenyls (III) and (II) arose in yields of 0.4% and 0.09%, respectively. Recrystallisation from heptane furnished the compounds with melting points at 229–230° and 198–202° (no depression on admixture of authentic compounds from previous work[1-3]).

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