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CYCLODIMERIZATION OF THE 1-METHYL-1,3-DIFERROCENYLALLYL CATION INTO 1,3,5-TRIFERROCENYL-4-(1-FERROCENYLETHENYL)CYCLOHEXENE

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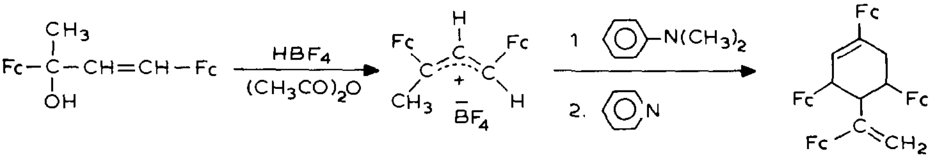
Summary

An unusual cyclodimerization reaction of the 1-methyl-1,3-diferrocenylallyl cation into 1,3,5-triferrocenyl-4-(1-ferrocenylethenyl)cyclohexene has been studied. Two isomeric compounds were isolated and their structures were established as 1,*r*3,*c*5-triferrocenyl-4-*t*-(1-ferrocenylethenyl)cyclohexene and 1,*r*3,*t*5-triferrocenyl-4-*c*-(1-ferrocenylethenyl)cyclohexene on the basis of ^{1}H NMR and ^{13}C NMR spectral data.

Ferrocenylalkyl, ferrocenylaryl and ferrocenylallyl cations are known to interact with nucleophiles as alkylating agents. Thus they alkylate dimethylaniline at the *p*-position while with pyridine they form the corresponding pyridinium salts [1–3].

We have studied the reaction of 1-methyl-1,3-diferrocenylallyltetrafluoroborate (IIa) with dimethylaniline and pyridine. The result was unexpected. Instead of the product of alkylation at the *p*-position the reaction mixture on interaction with dimethylaniline yielded two substances with isomeric 1,3,5-triferrocenyl-4-(1-ferrocenylethenyl)cyclohexene structures (III$_1$ and III$_2$) assigned on the basis of IR, mass, ^{1}H NMR and ^{13}C NMR spectra. The reaction with pyridine proceeds similarly (eq. 1).



(I) (IIa) (III$_1$, III$_2$)

(Fc = $C_5H_5FeC_5H_4$)

The structures of the compounds obtained were verified as follows. The mass spectra of both substances (*m/e* 422,844) indicated the dimeric nature of the

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reaction products. The IR spectra of III_1 and III_2 showed a band at 890 cm^{-1} characteristic of a terminal methylene group. In the ^{13}C NMR proton-decoupled spectra with total quenching of the spin–spin interaction with protons, the signals of four olefinic and four aliphatic carbon atoms were found for each compound; signals corresponding to four ferrocenyl groups were also present. The presence of two quaternary, one tertiary and secondary olefin carbon atoms and three CH and one CH_2 aliphatic groups was established by off-resonance spectra (see Table 1).

In the ^1H NMR spectra (250 MHz) resonances due to three olefin protons (4.7–6.5 ppm), four ferrocenyl groups (3.7–4.6 ppm) and five aliphatic protons (2.0–3.3 ppm) with corresponding integral intensities were found. The ^1H NMR spectral data fully agreed with the data of the ^{13}C NMR spectra.

The ^1H NMR spectra were analysed as follows. The presence of spin–spin interaction between separate protons was established and spin coupling constants were tentatively determined by means of homonuclear double-resonance. The data obtained on the chemical shifts and spin coupling constants (J(H–H)) were refined (for six protons of the cycle) by iteration. The remaining chemical shift and J(H–H) data were obtained directly from the experimental spectrum. The obtained values of

TABLE 1

^1H NMR AND ^{13}C NMR SPECTRAL DATA FOR THE 1,3,5-TRIFERROCENYL-4-(1-FERROCENYLETHENYL)CYCLOHEXENES III_1 AND III_2 [a]

Number (Fig. 2), atom or group	Isomer III_1			Isomer III_2		
	$\delta(^1H)$ [b]	$J_{m,n}$ (Hz)	$\delta(^{13}C)$ [c]	$\delta(^1H)$ [b]	$J_{m,n}$ (Hz)	$\delta(^{13}C)$ [c]
1	–	2,3 (2.76)	133.74	–	2,3 (3 27)	133.26
2	(6.4386)	2,4 (−0.02)	124 47	(6.39762)	2,4 (0.02)	123.39
3	(3.2492)	2,5 (0.05)	42.86	(3.2846)	2,5 (0.17)	37.47
4	(2.0095)	$2,6_x$ (−1.80)	57.85	(2.6252)	2,6 (−1 87)	50.79
5	(2.7211)	$2,6_y$ (−1.31)	39 58	(2.9316)	$2,6_y$ (−1.69)	35.10
6_x	(2.6098)	3,4 (8.98)	34.40	(2.9879)	3,4 (5 26)	32.00
6_y	(3.0201)	3,5 (−0.16)		(2 7886)	3,5 (−0.11)	
7	–	$3,6_x$ (3.04)	148.87	–	$3,6_x$ (2.85)	142.61
8	4.94	$3,6_y$ (2.22)	111.77	4.75	$3,6_y$ (2.12)	111 02
	5.41	4.5 (9.83)		5.22	4,5 (5 77)	
	3.91	$4,6_x$ (−0.40)	69.20	3.84	$4,6_x$ (−0.20)	68.34
	4.15	$4,6_y$ (0.06)	69.01	4 09	$4,6_y$ (0 13)	68.48
C_5H_5	4.17	$5,6_x$ (10.17)	68.29	4.19	$5,6_x$ (6.17)	68.77
	4.22	$5,6_y$ (4.63)	68 18	4.25	$5,6_y$ (4.66)	69.31
		$6_x,6_y$ (−16.83)			$6_x,6_y$ (−17.56)	
C_5H_4	3.76–	$8_x,8_y$ ±1.31	64.73–	3.95–	$8_x,8_y$ = ±1.24	64.20
	4.53		70.60	4.60		69.60
C_s	–		87.45			87 10
			89.13			87.80
			92.41			90.15
			93.55			94.25

[a] The spectra were measured on a Bruker WM-250 instrument for sample solutions in $CDCl_3$. ^1H and ^{13}C chemical shifts are accurate to ±0.01 and ±0.05 ppm, respectively. [b] $\delta(^1H)$ for internal $CHCl_3$ was chosen as 7.24 ppm (standard deviation for the chemical shifts and $J(H(2)-H(6)) \leqslant 0.08$ Hz for III_1 and $\leqslant 0.13$ Hz for isomer III_2). The results of the iterative refinements of the simulated spectra are given in parentheses. [c] $\delta(^{13}C)$ for $CDCl_3$ was chosen as 76.94 ppm.

the chemical shifts and spin coupling constants allowed the assignment of the ^{1}H NMR signals (Table 1).

The experimental and the respective calculated ^{1}H NMR spectra for both isomers (without ferrocene fragments) are shown in Fig. 1.

1,3,5-Triferrocenyl-4-(1-ferrocenylethenyl)cyclohexenes may exist as four diastereomers (Fig. 2). The values $J_{3,4}$, $J_{4,5}$ and $J_{5,6x} \approx 10$ Hz for isomer III$_1$ allow the structure 1,*r*3,*c*5-triferrocenyl-4-*t*-(1-ferrocenylethenyl)cyclohexene to be assigned to it. The given values of J(H–H) as well as the general stereochemical considerations allow us to consider isomer III$_1$ as fixed in conformation 1A. The 1B conformation does not make a significant contribution.

The structure of III$_2$ is more difficult to ascertain. Yet, it should be noted that the absence of $^3J > 6$ Hz in the ^{1}H NMR spectra indicates the existence of two conformers of III$_2$ with comparable contributions. Structure 4 does not conform to this requirement since the contribution of conformation 4A must be predominant in it. Of the two possible structures, 2 and 3, we are inclined to assign the structure 1,*r*3,*t*5-triferrocenyl-4-*c*-(1-ferrocenylethenyl)cyclohexene to isomer III$_2$, i.e. to attribute it to type 2 (Fig. 2).

After the analysis of the ^{1}H NMR data, measurement of the ^{13}C NMR spectra with selective heteronuclear decoupling from protons H(3) and H(4) was carried out. The signals of C$_{(3)}$–C$_{(5)}$ for both isomers were assigned (Table 1).

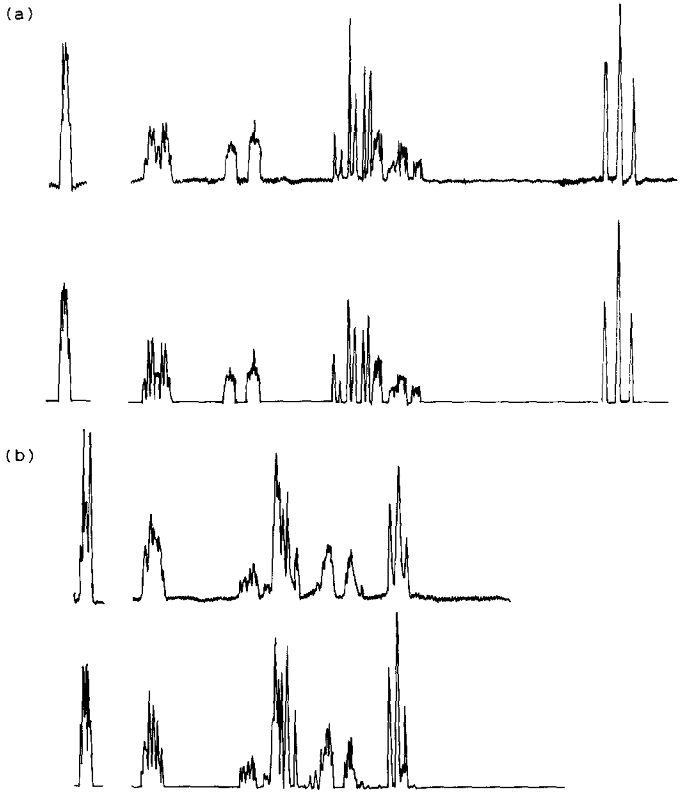
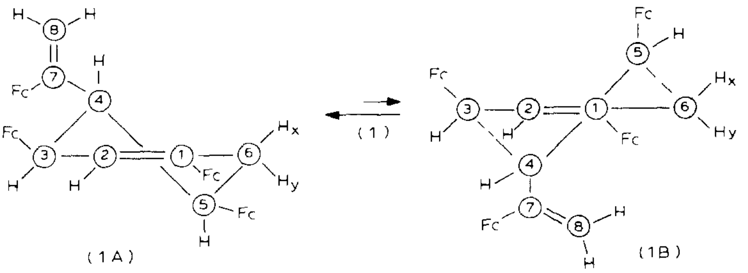
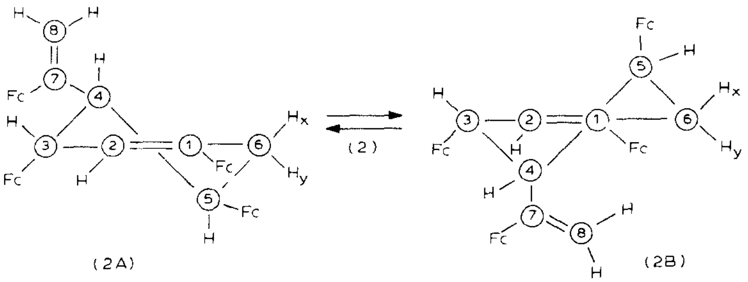


Fig. 1. Experimental and calculated spectra of compound III$_1$ (a) and III$_2$ (b).



1,*r*3, *c*5-Triferrocenyl-4-*t*-(1-ferrocenylethenyl)cyclohexene (III$_1$)



1,*r*3, *t*5-Triferrocenyl-4-*c*-(1-ferrocenylethenyl)cyclohexene (III$_2$)

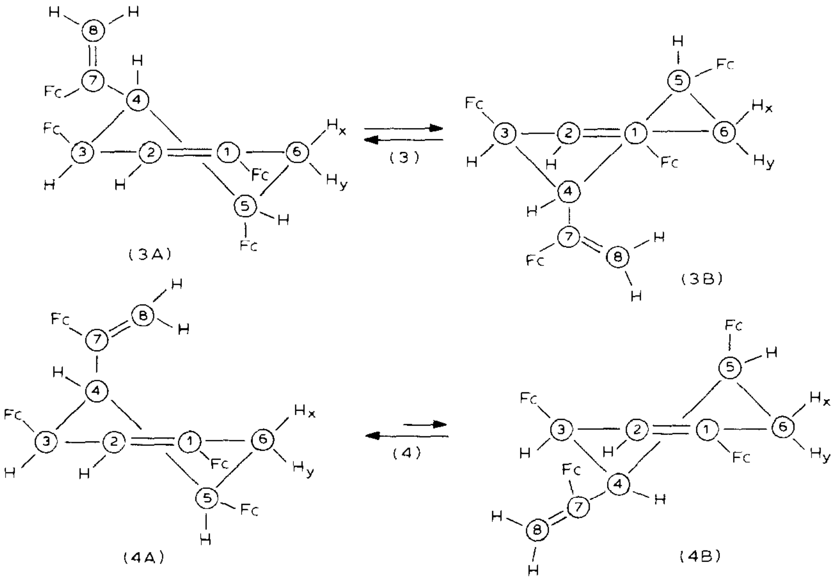
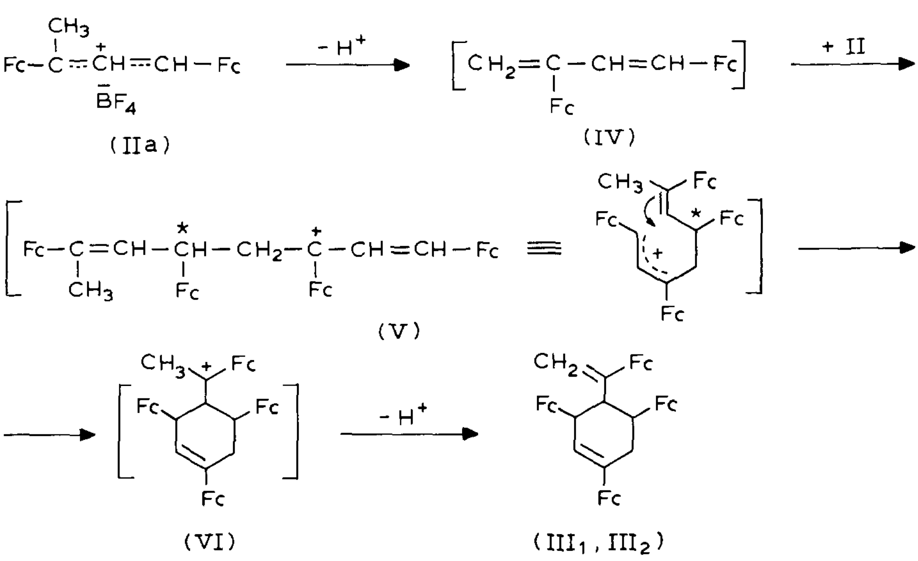


Fig. 2. Diastereomeric structures of compounds III$_1$ and III$_2$.

We suppose that the formation of III$_1$ and III$_2$ proceeds via an ionic mechanism with participation of ferrocenylallyl cations. The allyl cation in fluoroborate (IIa) is first deprotonized under the action of nucleophiles as in the case of α-ferrocenylcarbo cations [4] with the formation of intermediate 1,3-diferrocenyl-1,3-butadiene (IV). Diene IV is then alkylated by the allyl cation (II), with II being captured exclusively by the secondary cation centre thus giving rise to a new dimer allyl cation (V):



A similar dimerization process has been studied earlier in the case of α-ferrocenylalkylcarbo cations [5,6]. Furthermore, cation V alkylates the C=C bond intramolecularly with the formation of methylcyclohexenylferrocenylcarbo cation (VI); the latter is stabilized in compounds III_1, III_2, after a proton has been eliminated.

The readiness with which both isomers III_1 and III_2 are formed from carbinol I by the action of acetic acid is evidence in favour of this scheme. The total yield is almost quantitative. The deprotonation of the 1-methyl-1,3-diferrocenylallyl cation formed in acidic medium seems to proceed readily even under these conditions with further instant cyclodimerization. The increase in the acidity of the medium prevents deprotonization. Thus carbinol I solution in trifluoroacetic acid retains a bright green colour for a long time, while the ^1H NMR spectrum of the solution corresponds to that of the 1-methyl-1,3-diferrocenylallyl cation (IIb).

We have found that both III_1 and III_2 undergo fragmentation when treated with trifluoroacetic acid to form 1-methyl-1,3-diferrocenylallyl cation (IIb), which is indicated by ^1H NMR spectral measurements. This process is essentially the reverse of the cyclodimerization of the same cation described above. When trifluoroacetic acid is neutralized, e.g. by $NaHCO_3$ solution, an admixture of isomers III_1 and III_2 is obtained in the same ratio as before (1/3.5).

The formation of mainly two diastereomers in the approximately constant ratio 1/3 indicates the considerable stereoselectivity of the 1-methyl-1,3-diferrocenylallyl cation cyclodimerization reaction. This fact may be accounted for by stereochemical control operative during cation V cyclization since the asymmetric C^* atom is close to the $C_{(4)}$ asymmetric centre that is formed and thus determines the configuration at $C_{(4)}$. If this assumption is correct, the two diastereomers that are formed must exhibit the same mutual arrangement of substituents at $C_{(4)}$ and $C_{(5)}$, and isomer III_2 must have structure 2.

It should be noted that at this stage of our work the possibility of cyclodimerization of intermediate 1,3-diferrocenyl-1,3-butadiene (IV) by the Diels–Alder cycloaddition reaction may not be rejected. Isomer III_1 of type 1A would then correspond to the *exo*-adduct, while isomer III_2 of type 2 would correspond to the *endo*-adduct of diene synthesis.

Experimental

^1H NMR and ^{13}C NMR spectra were recorded on Bruker WM-250 and CXP-200 instruments (TMS-internal standard, $CDCl_3$). The iteration procedure and simulation of the ^1H NMR spectra were carried out by the PANIC program using an ASPEKT-2000 mini-computer.

I. 1-Methyl-1,3-diferrocenylallyl alcohol (I)

0.42 g of powdered ferrocenalacetylferrocene was added to CH_3Li/ether solution under stirring in argon. Stirring was continued for 30 min, the reaction mixture was then treated with 5% NaOH solution, and the ether layer was separated, washed with water and dried over $MgSO_4$. After elimination of ether the remainder was chromatographed (Al_2O_3; benzene/petroleum ether mixture, 1/1). 0.34 g (76%) of carbinol was obtained, m.p. 116–117 °C. ^1H NMR spectrum, δ ppm: 1.6 (s, 3H, CH_3); 2.24 (s, 1 H, OH); 4.10 (s, 5H, C_5H_5); 4.15–4.36 (m, 8H, C_5H_4); 4.23 (s, 5H, C_5H_5); 6.12 (d, 1H, CH, J 15.9 Hz); 6.35 (d, 1H, CH-Fe, J 15.9 Hz). Found: C, 65.69; H, 5.64; Fe, 25.53. $C_{24}H_{24}Fe_2O$ calcd.: C, 65.49; H, 5.49; Fe, 25.39%.

II. 1-Methyl-1,3-diferrocenylallyl cation (II)

(a) Borofluoride IIa. 0.44 g of allylcarbinol I solution in 10 ml of acetic anhydride was added to 5 ml of 40% HBF_4 in 20 ml of acetic anhydride. The mixture was stirred under argon for 1 h, then poured into 100 ml of absolute ether. The precipitate was filtered, washed with absolute ether, and dried in a vacuum-dessicator over P_4O_{10}. 0.43 g (84%) of 1-methyl-1,3-diferrocenylallyl cation borofluoride was obtained as a blue-green powder. ^1H NMR spectrum, δ (ppm): 1.98 (d, 3H, CH_3, J 1.3 Hz), 4.39, 4.52 (s, 10H, C_5H_5); 5.04, 5.11, 5.20, 5.66, 5.71 (m, 8H, C_5H_4); 6.10 (dq, 1H, CH, J_d 14 Hz, J_q 1.3 Hz); 8.54 (d, 1H, CH–Fe, J 14 Hz).

(b) Trifluoroacetate IIb. Several drops of CF_3COOH were added to 0.1 g of allyl alcohol I solution in 1 ml of $CDCl_3$. A bright green coloured solution was obtained. The ^1H NMR spectrum of IIb was identical to that of borofluoride IIa.

III. 1,3,5-Triferrocenyl-4-(1-ferrocenylethenyl)cyclohexene (III)

(a) 0.25 g of 1-methyl-1,3-diferrocenylallyl cation borofluoride was carefully pulverized with 0.5 ml of dimethylaniline. After 30 min the mixture was diluted with 50 ml of ether, washed with water, 1% HCl solution, and water; the organic layer was separated, dried over $CaCl_2$, and the solvent evaporated. The residue was chromatographed (Al_2O_3; benzene/petroleum ether mixture, 1/1). 0.18 g (85%) of a mixture of dimer products III_1 and III_2 was obtained, m.p. 195–196 °C, isomer ratio (by ^1H NMR spectra) ~ 3/1, respectively. Found: C, 68.37; H, 5.40; Fe, 25.99. $C_{48}H_{44}Fe_4$ calcd.: C, 68.28; H, 5.25; Fe, 26.47%.

Pure isomer III_1 was isolated by multiple recrystallizations from ether solution, m.p. 208–209 °C. Mass spectrum, *m/e*: 56, 121, 186, 211, 236, 300, 356, 422, 631, 658, 844. Found: C, 67.94; H, 5.23; Fe, 26.93%.

Recrystallization of the remainder from n-heptane yielded pure isomer III_2, m.p. 236–237 °C, mass spectrum *m/e*: 56, 121, 186, 211, 236, 300, 356, 422, 631, 658, 844. Found: C, 68.03; H, 5.34; Fe, 26.67%.

(b) 0.51 g of solid borofluoride IIa was added to a solution of 1 ml of pyridine in 25 ml of absolute ether. The mixture was stirred for 30 min, washed with water, the organic layer was separated, dried, and the solvent evaporated. The residue was chromatographed. 0.38 g (86%) of dimers III_1 and III_2 was obtained in the ratio ~ 1/3.5; m.p. 195–196 °C.

(c) 2 ml of acetic acid was added to a solution of 1 g of carbinol I in 50 ml of CH_2Cl_2. The yellow solution was stirred at room temperature for 1 h, then washed with water several times, then with 1% $NaHCO_3$ solution, and finally with water. After standard treatment, 0.85 g (90%) of a mixture of the cyclodimerization products III_1 and III_2 was obtained in the ratio ~ 1/3.

IV. Fragmentation of 1,3,5-triferrocenyl-4-(1-ferrocenylethenyl)cyclohexenes III_1 and III_2

The fragmentation was carried out by adding trifluoroacetic acid to a solution of 0.05 g of each isomer in $CDCl_3$. The formation of allyl cations IIb in the solutions was indicated by the ^1H NMR spectra.

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