0.17; retention time for I, 105 sec at 50°C, for VII, 180 sec at 105°C; IR spectra of I, identical; refractive index of I, n_D^{20}, 1.5052 (from data in [1], n_D^{20} is 1.5052).

We investigated the products of the reaction of salts of 1-methyl- and 2-ethyl-5-nitroaminotetrazole and salts of 5-nitroaminotetrazole with ethyl iodide by means of TLC (Silufol plates, 11:3:1 benzene/hexane/ether eluent, developed in iodine vapor). We measured the IR spectra and determined the refractive indices of the individual N-isomers of VI. The characteristics of all of the samples were the same: R_f VI 0.64; IR spectrum of VI identical, refractive index of VI, n_D^{20}, 1.4890.

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TWOFOLD REACTIVITY OF 1,2-DISUBSTITUTED DIHYDRO-N-HETEROAROMATIC SYSTEMS.

10.* SYNTHESIS AND AROMATIZATION OF FERROCENE-CONTAINING HANTZSCH ESTERS

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UDC 547.827'172:543.87:541.124

1-Ferrocenylphenyl-4-aryl(furyl)-2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridines and 4-ferrocenyl-2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridines (Hantzsch esters) have been prepared, and their reactions with triphenylcarbenium and 1-oxo-2,2,6,6-tetramethyl-piperidinium perchlorate salts have been studied. Treatment with triphenylmethyl perchlorate results in oxidation of the ferrocenyl substituent to the ferrocenium cation, whereas treatment with the oxoammonium cation results in aromatization and the formation of salts containing a pyridinium cation and a neutral ferrocene ring. A 4-ferrocenyl-containing Hantzsch ester which was unsubstituted at the nitrogen atom constituted a single exception to this trend; it could be aromatized only upon treatment with sulfur.

The twofold reactivity of 1,2(4)-disubstituted 1,2(4)-dihydrohetero-aromatic compounds with respect to aromatization reagents has been described previously [2], and was found to depend on the relationship between the electrophilicity and oxidizing ability of the aromatizing agent. Strong oxidizing agents with weak electrophilic characteristics, such as 1-oxo-2,2,6,6-tetramethylpiperidinium perchlorate [2], direct the reaction along the oxidative pathway, leading to loss of hydrogen and preservation of the α-substituent [3-5], whereas strong electrophiles which are not strong oxidizing agents, such as triphenylcarbenium perchlorate, direct the reaction along an electrophilic pathway, resulting in cleavage of anion-stabilizing substituent groups, such as indole or CH-acids [2].

It was therefore of interest to us to examine the reactivity of these two cations on ferrocenyl-containing Hantzsch esters, since it is well known that aromatization of ferrocenyl-containing Yanov σ-complexes [6] or 1,4-dihydropyridines [7] involves preliminary oxidation

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*For Communication 9, see [1].

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0009-3122/86/2208-0886$12.50

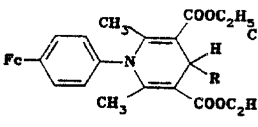
TABLE 1. Properties of Newly Synthesized Substances

Compound	mp,* °C	Found, %			Molecular formula	Calc., %			Yield, %
		C	H	N		C	H	N	
Ia	212—213	65,9	5,6	4,6	$C_{35}H_{35}FeN_2O_6$	66,1	5,5	4,4	75
Ib	174—174,5	65,7	5,4	4,3	$C_{35}H_{35}FeN_2O_6$	66,1	5,5	4,4	28
Ic	223—225	65,8	5,6	4,2	$C_{35}H_{35}FeN_2O_6$	66,1	5,5	4,4	72
Id	166—166,5	68,4	5,7	2,5	$C_{33}H_{33}FeNO_5$	68,4	5,7	2,4	50
Ie	155—156	69,9	6,2	2,1	$C_{36}H_{38}FeNO_5$	69,7	6,2	2,3	27
II	210—212	63,3	6,3	3,3	$C_{23}H_{27}FeNO_4$	63,1	6,2	3,2	80
III	142—143	63,5	6,4	3,4	$C_{24}H_{29}FeNO_4$	63,8	6,5	3,1	82
IVa	241—242	67,0	4,2	6,6	$C_{23}H_{18}FeN_2O_2$	67,3	4,4	6,8	97
IVb	118—119	67,2	4,3	6,8	$C_{23}H_{18}FeN_2O_2$	67,3	4,4	6,8	93
IVc	144—145	67,1	4,3	6,6	$C_{23}H_{18}FeN_2O_2$	67,3	4,4	6,8	98
IVd	148—149	71,0	4,6	3,9	$C_{21}H_{17}FeNO$	70,9	4,8	3,9	77
IVe	189—190	72,7	5,3	3,4	$C_{24}H_{21}FeNO$	72,9	5,4	3,5	88
IVf	268—270	72,3	4,8	3,6	$C_{23}H_{19}FeNO$	72,5	5,0	3,6	83
IVg	213—214	73,3	5,5	6,8	$C_{25}H_{24}FeN_2$	73,5	5,9	6,9	90
IXa	204—205	56,9	4,7	3,9	$C_{35}H_{34}ClFeN_2O_{10}$	57,3	4,7	3,8	50
IXb	196—197	57,1	4,5	4,0	$C_{35}H_{34}ClFeN_2O_{10}$	57,3	4,7	3,8	47
IXd	217—218	58,3	4,8	2,1	$C_{33}H_{32}ClFeNO_9$	58,5	4,8	2,1	50
IXe	197—198	60,5	5,2	2,1	$C_{36}H_{35}ClFeNO_9$	60,2	5,0	2,0	45
X	194—195	51,9	4,9	2,5	$C_{24}H_{28}ClFeNO_8$	52,4	5,1	2,6	50
XI	217—219	60.2	4,8	2,9	$C_{24}H_{24}ClFeNO_4$	59,8	5,0	2,9	65
XII	93—94	63,3	5,5	3,0	$C_{23}H_{25}FeNO_4$	63,4	5,8	3,2	20

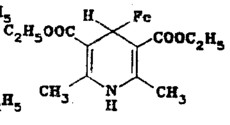
*Compounds Ia-e were crystallized from propanol, compound II, from benzene.

of the ferrocenyl substituent to a ferrocenium cation, which is not susceptible to cleavage, and which also, because of its strongly electron-withdrawing character, inhibits loss of hydrogen from geminal positions relative to it, whether by an ionic or SET mechanism. It would therefore seem likely that aromatizing agents which induce aromatization by an ionic mechanism involving cleavage of a substituent would not be effective in the case of the Hantzsch esters. In order to verify this hypothesis, we have investigated the reactivity of both triphenylcarbenium and 1-oxo-2,2,6,6-tetramethylpiperidinium perchlorates with ferrocenyl-containing Hantzsch esters, namely, 1-p-ferrocenylphenyl-4-aryl(furyl)-2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridines (Ia-e), and 4-ferrocenyl-2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridines (II, III).

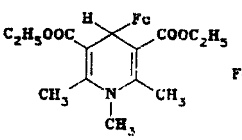
Compounds Ia-e were prepared according to a known method [8] by treatment of ferrocenylphenylamine with aromatic and heterocyclic aldehydes and acetoacetic ester. This synthesis is conveniently carried out in two stages: the first stage involves formation of the corresponding azomethines IVa-g, which are formed in excellent yield in the reactions of p-ferrocenylphenylamine with aldehydes containing both electron donating as well as electron withdrawing substituents (Table 1), and the second stage involves condensation of the azomethines containing electron withdrawing substituents with acetoacetic ester to give N-p-ferrocenylphenyl-substituted Hantzsch esters Ia-e (Table 1). Electron donating substituents on the aldehyde component of the azomethine inhibit this second reaction stage.



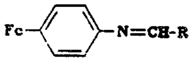
Ia-e



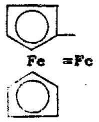
II



III

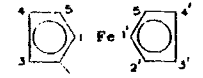


IVa-g



a $R = p\text{-}NO_2C_6H_4$—; b $R = m\text{-}NO_2C_6H_4$—; c $R = o\text{-}NO_2C_6H_4$—; d R = 2-furyl-; e $R = p\text{-}CH_3OC_6H_4$—; f $R = p\text{-}HOC_6H_4$—; g $R = p\text{-}(CH_3)_2NC_6H_4$—

TABLE 2. Spectral Characteristics of Compounds I-III, and IX-XII

Compound	PMR spectrum, δ, ppm, (DMSO-D6)								UV spectrum, λ max, nm (log ε)	IR spectrum, ν max, cm⁻¹ (% absorption), in the regions 1800-1500 and 3600-3300 cm⁻¹
	3,5 $COOC_2H_5$		2,6-CH_3 (s 6H)	4H (s, 1H)			N–R, R=H, R=CH_3, R=Ph	4R', R'= =Ra-e		
	CH_3 (t 6H)	CH_2 (q, 4H)			1,3-H (t 2H); 4,5-H (t 2H)	1',2',3',4',5'-H (s, 5H)				
Ia	1,17	4,05	2,06	5,14	4,87, 4,41	4,03	7,23 (d 2H), 7,67 (d, 2H)	7,59 (d,2H), 8,23 (d, 2H)	210 (4,83), 247 (4,49), 288 (4,41), 330 **sh** (3,5), 472 (2,04)	1700 (85), 1640 (50), 1580 (47), 1527 (71)
Ib	1,17	4,08	2,07	5,12	4,89, 4,41	4,03	7,25 (d, 2H), 7,69 (d, 2H)	8,16 (d,1H), 7,6—8,1 (m, 3H)	211 (4,66), 248 (4,62), 276 (4,49), 340 (3,98), 460 (3,0)	1700 (82), 1695 (35), 1650 (66), 1587 (68), 1533 (85)
Ic	1,09	3,99	1,96	5,62	4,89, 4,41	4,07	7,32 (d, 2H), 7,69 (d 2H)	7,37—7,87 (m, 4H)	212 (4,65), 247 (4,53), 287 (4,35), 330 **sh** (4,0), 465 (3,17)	1700 (92), 1650 (67), 1585 (70), 1515 (85), 1530 (80)
Id	1,21	4,12	2,04	5,16	4,86, 4,39	4,02	7,16 (d, 2H), 7,65 (d, 2H)	6,01 (d, 1H), 6,34 (q, 1H), 7,53 (q, 1H)	212 (4,54), 247 (4,4), 286 (4,27), 345 (4,1), 468 (3,11)	1695 (86), 1685 (64), 1610 (49), 1585 (62), 1525, 1510 д (55)
Ie	1,17	4,07	2,02	4,97	4,87, 4,40	4,03	6,87 (d, 2H), 7,22 (d, 2H)	7,66 (d,2H), 7,18 (d,2H), 3,73 (s, 3H)	212 (4,8), 250 (4,7), 287 (4,6), 350 (4,02), 462 (2,3)	1695 (76), 1640 (58), 1570 (57), 1523 (56)
II (in $CDCl_3$)	1,42	4,60	2,52	5,30	4,45, 4,34	4,52	9,87 (s 1H)		211 (4,52), 240 (4,36), 280 (4,0), 337 (3,9), 456 (2,5)	3440 (82), 3395 (42), 1700 (90), 1655 (92)
III	1,28	4,17	2,36	4,84	3,95, 3,82	4,03	3,14 (s 3H)		209 (4,6), 241 (4,3), 267 (4,1), 338 (3,8), 458 (2,7)	1680 (93), 1640 пл. (78), 1585 (55)
IXa	0,94	4,13	2,47 (in DMSO)		4,99, 4,49	4,09	8,49 (d, 2H), 7,64 (d, 2H)	7,64 (d,2H), 7,94 (d, 2H)	210 (4,9), 252 **sh** (4,5), 286 (4,7), 472 (2,8)	1720 (73), 1600 (33), 1510 (60)
IXb	0,93	4,15	2,47 (in DMSO)		4,98, 4,49	4,09	7,94 (d, 2H), 7,61 (d, 2H)	8,52 (d, 1H), 8,15 (s, 1H), 7,89 (m, 2H)	207 (4,8), 251 (4,5), 275 (4,7), 335 **sh** (3,8), 467 (2,8)	1736 (80), 1625 (54), 1523 (65)
IXd	1,25	4,45	2,36		4,98, 4,48	4,07	7,63 (d, 2H), 7,89 (d, 2H)	6,92 (q, 1H), 7,18 (d, 1H), 8,27 (d, 1H)	207 (4,6), 248 (4,1), 287 (3,9), 357 (4,4), 472 (3,8)	1737 (82), 1645 (63), 1575 (58), 1525 (44)
IXe	0,98	4,16	2,41		4,98, 4,48	4,08	7,92 (d, 2H), 7,66 (d, 2H)	7,28 (d,2H), 7,23 (d,2H), 3,85 (s, 3H)	210 (4,7), 250 **sh** (4,5), 287 (4,3), 356 (4,1), 480 (3,4)	1738 (84), 1624 (74), 1533 (55)
X	1,30	4,49	2,65		4,84, 4,69	4,27	3,97 (s, 3H)		210 (4,5), 288 (4,3), 316 (4,2), 438 (3,7), 568 (3,5)	1735 (82), 1584 (75), 1542 (44)
XI			2,36		4,96, 4,46	4,06	7,48 (d, 2H), 7,87 (d, 2H)	2,61 (s, 3H), 7,92 (s, 2H)	209 (4,7), 250 **sh** (4,6), 281 (4,8), 352 **sh** (3,6), 464 (3,1)	1650 (63), 1570 (32), 1520 (58)
XII	1,27	4,35	2,41		4,50 (s, 4H)	4,17			207 (4,4), 284 (4,0), 361 (3,1), 473 (2,7)	1727 (85), 1595 (34), 1550 (57)

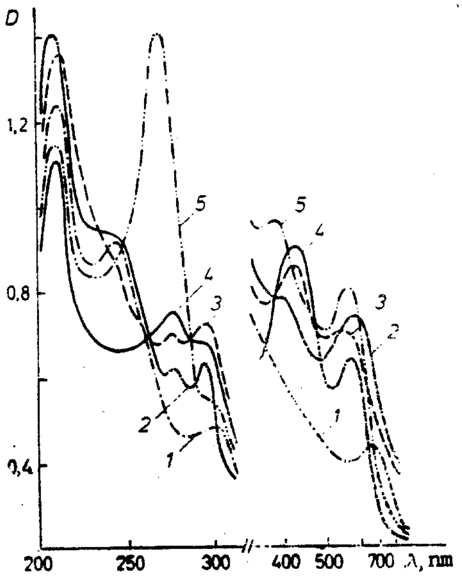


Fig. 1

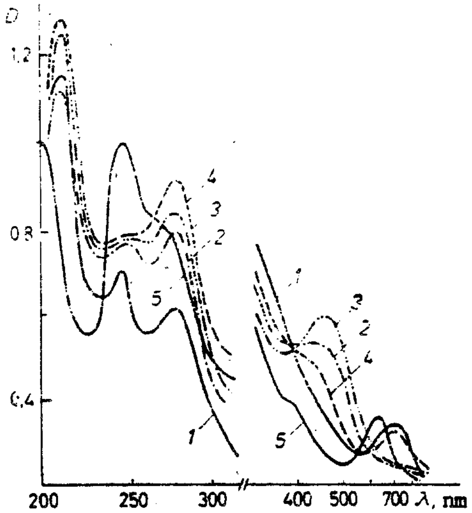
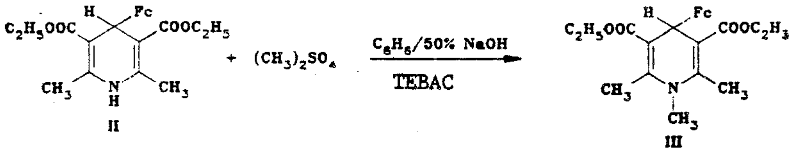


Fig. 2

Fig. 1. Electronic absorption spectrum (in CH_3CN). Aromatization of 1-p-ferrocenylphenyl-2,6-dimethyl-3,5-diethoxycarbonyl-4-p-nitrophenyl-1,4-dihydropyridine (Ia) with 1-oxo-2,2,6,6-tetramethylpiperidinium perchlorate (VIII). 1) Immediately after mixing of the reagents (Va); 2) after 45 min; 3) after 1 h and 30 min (IXa); 4) dication (XVIIIa); 5) ferrocenium perchlorate (in 0.1 N H_2SO_4).

Fig. 2. Electronic absorption spectrum (in CH_3CN). Aromatization of 4-ferrocenyl-1,2,6-trimethyl-3,5-diethoxycarbonylpyridine (III) with 1-oxo-2,2,6,6-tetramethylpiperidinium perchlorate (VIII). 1) Immediately after mixing of the reagents (VII); 2) after 18 h; 3) after 46 h; 4) after 82 h (X); 5) dication XIX.

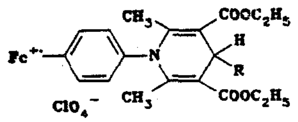
We have found that the Hantzsch ester II, obtained according to [9], can be easily alkylated at the nitrogen atom with either methyl iodide or dimethyl sulfate under phase transfer conditions with an equimolar amount of triethylbenzylammonium chloride (TEBAC) in benzene—50% NaOH to give compound III:

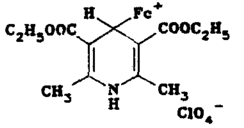


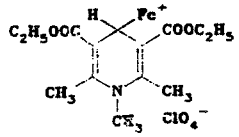
This newly discovered alkylation method is of preparative interest since it is well documented that Hantzsch esters containing 3,5-diethoxycarbonyl groups undergo alkylation at nitrogen with great difficulty and then only in the presence of strong bases, such as sodium hydride [10].

The UV, IR, and PMR spectra of the newly synthesized compounds I-III are fully consistent with their proposed structures (Table 2). The electronic spectra of compounds Ia-e differ from the spectra of N-substituted Hantzsch esters with analogous substituents [11] only by the presence of absorption bands due to the ferrocenyl ring at 330-350 nm and 460-470 nm. The IR spectra of these compounds contain a set of intense bands in the 1500-1700 cm^{-1} region, which is characteristic of mixed ester functional groups, and also bands at 3100, 1110, and 830 cm^{-1}, which can be assigned to ferrocene-group absorptions [12].

Treatment of compounds I-III with triphenylmethyl perchlorate in acetonitrile resulted in the formation of the 1,4-dihydropyridines V-VII, in which the ferrocene rings have been oxidized to the ferrocenium cation stage:

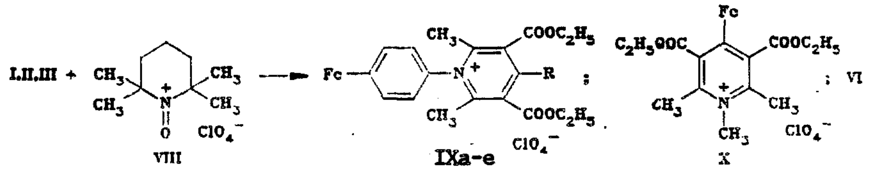

Va-e


VI


VII

We were unsuccessful in achieving aromatization of these substances using triphenylmethyl perchlorate, despite many attempts. The electronic spectra of compounds V-VII formed in the above reactions are missing the bands in the visible region corresponding to absorption by the ferrocene ring, and contain a new absorption maximum which is characteristic of the ferrocenium cation (Figs. 1 and 2). The only salts which we were able to isolate in the crystalline state corresponded to compounds VI and VII; the IR spectra of these compounds were practically identical with those of the starting materials, namely compounds II and III, with the exception of the appearance of a band due to the perchlorate anion at 1100 cm^{-1}, whereas their PMR spectra proved to be unresolvable as a consequence of the presence of the paramagnetic ferrocenium cation. Salts VI and VII could be easily reduced to their dihydropyridine precursors II and III with solutions of base or ammonia; this is a well known [13] reaction of the ferrocenium cation. Salts Va-e were found to exist in acetonitrile solution for a short time, although attempted isolation resulted in decomposition and formation of iron salts.

Treatment of compounds I-III with 2,2,6,6-tetramethyl-1-oxopiperidinium perchlorate (VIII) resulted in a variety of reaction paths: reactions involving compounds Ia-e and III resulted in formation of the corresponding pyridinium salts IXa-e and X, whereas in the case of compound II, containing an unsubstituted nitrogen atom, aromatization did not occur, and salt VI was isolated:

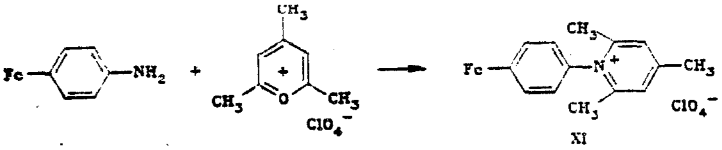

VIII

IXa-e

X

The UV spectra of the pyridinium salts IXa-e differ from those of the dihydropyridine precursors Ia-e with respect to the extinction coefficient of the absorption band at 250 nm, which is significantly reduced (Table 2).

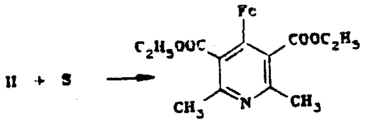
The structures of salts IX were confirmed by comparison of their spectral characterisitcs with those of salt XI, whose structure is known, and which was prepared by the reaction of p-ferrocenylphenylamine with 2,4,6-trimethylpyrilium perchlorate:


XI

It was found that these salts exhibit UV absorption maxima at the same wavelength (Table 2).

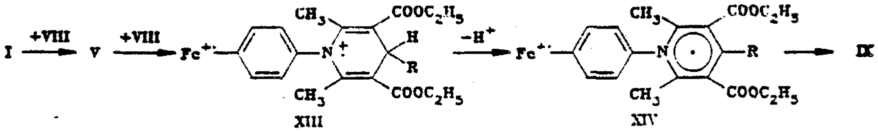
The PMR spectra of salts IXa-e do not contain signals due to the proton in the 4-position, and the signals of the 2,6-methyl groups are shifted downfield (relative to their precursors), just as was found in the case of the PMR spectrum of XI, which further confirms their structure (Table 2).

We note that, in contrast to the behavior of dihydropyridine derivative III, the Hantzsch ester II containing an unsubstituted NH group could only be aromatized in the presence of elemental sulfur, resulting in the formation of 4-ferrocenyl-2,6-dimethyl-3,5-diethoxycarbonylpyridine (XII).



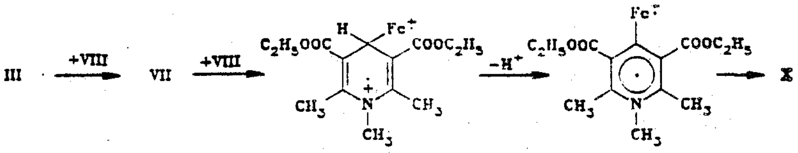
XII

Spectrophotometric study of the aromatization reactions of dihydropyridines I-III revealed that preliminary oxidation of the ferrocene group to a ferrocenium cation occurred in all cases to give the salts V-VII, and that the pyridinium portion of the spectra did not change at all during this stage; this indicates that intramolecular oxidation of dihydropyridine rings by means of the ferrocenium cations was not taking place. Further reaction apparently involves oxidation of the dihydropyridine ring by means of excess perchlorate salt VIII to give the dication diradical species XIII, which loses a proton and undergoes either intramolecular or intermolecular [14] oxidation by the ferrocenium cation to generate the final product of the reaction, compound IX:



XIII XIV

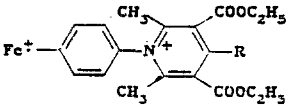
Aromatization of the Hantzsch ester III occurs in an analogous manner. The presence of an intramolecular oxidation-reduction sequence in this reaction is supported by the observation that the UV spectrum of salt X, in addition to exhibiting a hypsochromic shift of the ferrocene absorption at 438 nm, also displays a new maximum at 568 nm, which can be assigned to a charge transfer transition between the ferrocene group and the pyridinium ring (Fig. 2).



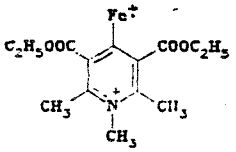
XV XVI

A similar reaction pathway for aromatization of all of the compounds I-III is reasonable in light of the recently published data [15] concerning the mechanism of dehydrogenation of α-hydrogen containing substituted ferrocenes using triphenylmethyl perchlorate.

Another reaction pathway involving intermediate formation of the dications XVII and XVIII is possible; these dications would be expected to form in cases where oxidation of the cation-biradicals XIV and XVI takes place not via the ferrocenium cations, but rather as a consequence of the presence of excess oxoammonium salt VIII. The reaction products IX and X could then be formed as a result of partial reduction of the dications XVII and XVIII by means of either the starting materials I, III or the reaction media.



XVII



XVIII

The authors of a study of the aromatization of ferrocene-containing anionic σ-complexes of trinitrobenzene [6] have postulated an analogous mechanistic path; they assumed that reduction of the (initially) formed ferrocenium cation occurs by means of the σ-complex precursor. Spectrophotometric monitoring of our reactions indicated that the ferrocene rings in the starting materials underwent oxidation immediately after mixing of the reagents (Fig. 1, 2). Treatment of the salts IXa-e and X with equimolar amounts of the oxidant VIII resulted in the formation of dications of structure XVIII and XIX, according to their UV spectra; the dications proved to be unstable in air, but in acetonitrile solutions these materials did not undergo reduction by the medium to give the salts IX and X even after extended storage (Figs. 1, 2).

We have found that aromatization of ferrocene-containing Hantzsch esters occurs via an SET mechanism; the first step of the reaction involves oxidation of the ferrocenyl fragment, and the probability of formation of the final reaction product depends on the oxidizing ability of the aromatizing agent.

EXPERIMENTAL

IR spectra were recorded on a Specord 75-IR spectrophotometer using KBr pellets, UV spectra were obtained on a Specord UV-VIS spectrophotometer in acetonitrile solutions, and PMR spectra were taken on a Bruker WH-90 spectrometer with HMDS as internal standard. Sample purities and the extent of reactions were followed by TLC analysis on Silufol UV-254 plates using chloroform–hexane–acetone (9:7:2) and iodine visualization. The properties of the newly synthesized compounds are reported in Tables 1 and 2.

p-Ferrocenylphenylamine was prepared according to [16], 2-formylferrocene according to [17].

p-Ferrocenylphenylazomethines IVa-g (General Method). A solution of 10 mmole of p-ferrocenylphenylamine and 10 mmole of the appropriate aldehyde in 20 ml of ethanol was refluxed for 1-2 h, cooled, and the precipitate was filtered and recrystallized from ethanol.

1-p-Ferrocenylphenyl-4-aryl(furyl)-2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridines (Ia-e). These are prepared according to [8] by reaction of azomethines IVa-e with acetoacetic ester. 4-Ferrocenyl-2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridine (II). This compound was obtained according to method [9] by reaction of 2-formylferrocene with ethyl β-aminocrotonate in the presence of ammonium carbonate.

1,2,6-Trimethyl-4-ferrocenyl-3,5-diethoxycarbonyl-1,4-dihydropyridine (III). A solution of 1 g (2 mmole) of compound II in 40 ml of benzene was treated with 0.46 g (2 mmole) of TEBAC, 15 ml of a 50% aqueous solution of NaOH, and 0.8 g (4 mmole) of dimethyl sulfate. The mixture was stirred for 2 h at 50-60°C, and then an additional hour at room temperature; the layers were then separated and the benzene layer was washed with saturated KCl solution, water, and finally dried over $MgSO_4$. The solvent was evaporated and the residue was recrystallized from propanol. Yield, 0.81 g (82%), mp 142-143°C. Alkylation of compound II with methyl iodide proceeded in an analogous manner. In that case the yield after 12 h reaction time (heating and stirring) was 35%.

1-p-Ferrocenylphenyl-4-aryl(furyl)-2,6-dimethyl-3,5-diethoxycarbonylpyridinium Perchlorates (IXa-e). General Method. A solution of 0.24 mmole of oxidant VIII in 5 ml of dry acetonitrile under an argon atmosphere was treated with 0.16 mmole of compound Ia-e and stirred for 1 h to 1 h and 30 min at 20°C. The reaction mixture was diluted with 150 ml of dry ether, and the resulting precipitate of salt IXa-e was filtered and recrystallized from dry methanol.

p-Ferrocenylphenyl-2,4,6-trimethylpyridinium Perchlorate (XI). A mixture of 0.4 g (1.8 mmole) of 2,4,6-trimethylpyrilium perchlorate and 1 g (3.6 mmole) of p-ferrocenylphenylamine in 20 ml of ethanol was refluxed for 1 h, cooled, and diluted with 50 ml of ether; the resulting precipitate was filtered and recrystallized from propanol.

4-Ferrocenyl-1,2,6-Trimethyl-3,5-diethoxycarbonylpyridinium Perchlorate (X). A solution of 0.11 g (0.44 mmole) of oxidant VIII in 3 ml of dry acetonitrile under argon was treated with 0.1 g (0.22 mmole) of compound III. The solution was heated to 50°C, stirred for 30 min, and then maintained at room temperature an additional hour prior to dilution with 100 ml of dry ether; the resulting precipitate was filtered and recrystallized from dry methanol.

4-Ferrocenyl-2,6-dimethyl-3,5-diethoxycarbonylpyridine (XII) A mixture of 0.5 g (1.2 mmole) of compound II and 0.12 g (3.6 mmole) of elemental sulfur was fused at 190-210°C and stirred (at this temperature) for 45 min, then cooled to room temperature and extracted with petroleum ether. After solvent removal and column chromatography on silica gel (with chloroform–hexane–acetone (9:7:2) eluent) pyridine XII was isolated and subsequently recrystallized from methanol.

2,6-Dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridine-4-ferrocenium Perchlorate (VI). A solution of 0.15 g (0.44 mmole) of triphenylmethyl perchlorate in 3 ml dry acetonitrile was treated with 0.19 g (0.44 mmole) of dihydropyridine II and stirred for 30 min; the solution was filtered and 75 ml of dry ether was added. The resulting green crystals were twice reprecipitated from acetonitrile with ether. Yield, 0.15 g (63%), flash point 185-187°C. IR spectrum: 730 s, 810 m, 1020 m, 1100 vs, 1210 s, 1288 m, 1310 m, 1370 m, 1450 w, 1490 s, 1645 m, 1680 vs, 1700 s, 2940 w, 3110 m, 3430 s cm^{-1}. UV spectrum, λ_{max} (log ε): 208 (4.4), 240 (4.3), 277 (3.8), 333 (3.5), and 644 nm (2.1).

1,2,6-Trimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridine-4-ferrocenium Perchlorate (VII). This was prepared in an analogous manner to that described above for compound VI from 0.1 g (0.22 mmole) of compound III and 0.075 g (0.22 mmole) of triphenylmethyl perchlorate. Yield, 0.06 g (50%), flash point 115-116°C. IR spectrum: 810 m, 970 w, 1010 m, 1106 vs, 1207s, 1265 m, 1375 m, 1487 s 1545 m, 1585 s, 1647 m, 1700 vs, 2946 w, 3010 w cm^{-1}. UV spectrum, λ_{max} (log ε): 210 (4.5), 242 (4.4), 336 (4.0), and 660 nm (2.9).

Elemental analyses of compounds VI and VII could not be obtained due to their severe detonating capacity.

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