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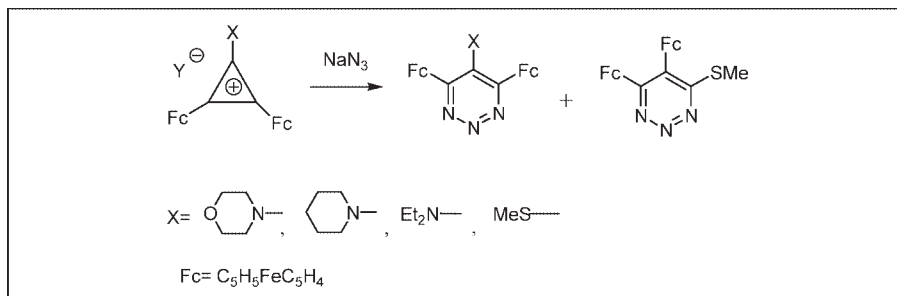
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The reactions of 1-amino-2,3-diferrocenylcyclopropenylum tetrafluoroborate (**5a–c**) or 2,3-diferrocenyl-1-methylthiocyclopropenylum iodide with sodium azide afford 5-amino-4,6-diferrocenyl-1,2,3-triazines (**7a–c**) or 5-methylthio-4,6-diferrocenyl- and 4-methylthio-5,6-diferrocenyl-1,2,3-triazines (**8a** and **8b**), respectively. Their structures were established using spectroscopic methods and that of compound **8a** was confirmed using X-ray diffraction analysis. Triazines **5a–c** react with alkyl iodides to yield N(2)- and N-alkyl-C(5)-derivatives. Their alkaline hydrolysis results in 2-methyl-4,6-diferrocenyl-2,5-dihydro-1,2,3-triazin-5-one (**16**) and 4,6-diferrocenyl-5-hydroxy-1,2,3-triazine (**17**). J.

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INTRODUCTION

The study of 1,2,3-triazines has been on-going at least since the early 1970s [1–6]. It is significant that the chemistry of this heterocyclic system is relatively underdeveloped. 1,2,3-Triazines are of particular interest as potential azete precursors [3,7–10]. The first thermodynamically stable trisubstituted azetes **1a** and **1b** with electron-withdrawing groups have been prepared by pyrolysis and photolysis of the corresponding 4,5,6-trisubstituted 1,2,3-triazines [3,9–11] (Scheme 1).

The ability of electron-density-deficient 1,2,3-triazine systems to interact with nucleophilic reagents, such as the Grignard reagents, electron-rich alkenes, and dienes, is also of interest [12–15]. Thus, 4,6-disubstituted 1,2,3-triazine **2a** undergoes nucleophilic attack at the N₍₂₎ and C₍₅₎ atoms of the heterocycle to yield 2,5-dihydro-1,2,3-triazines **3a** and **4a**, whereas 4,5,6-trisubstituted 1,2,3-triazine **2b** affords adducts **3b,c** exclusively upon nucleophilic attack at N₍₂₎ (Scheme 2).

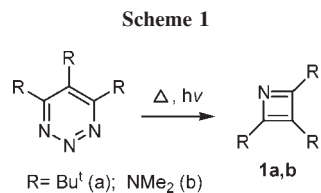
In addition to these reactions of 1,2,3-triazines, pyrolysis and photolysis resulting in substituted alkynes and

carbonitriles of mononitrogenous heterocycles are documented [2,4,9]. As bases, they form quaternary salts upon alkylation with alkyl halides at N₍₂₎ [16].

On the whole, compounds of the 1,2,3-triazine series are little studied in both the synthetic and practical aspects.

Ferrocenyl-substituted 1,2,3-triazines have not hitherto been described. The interest in these compounds may stem from the peculiarities of their chemical behavior due to the mutual effects of the ferrocene system and the heterocyclic fragment [17]. These effects may result in the emergence of diverse valuable properties, such as biological activity, dyeing ability, possible use as propellant additives or light-sensitive materials, and redox switching receptors in supramolecular chemistry, which has previously been observed for a number of heterylferrocenes [17].

In continuation of our studies in the field of diferrocenyl-substituted cyclopropenylum cations, we describe here the use of the latter for the synthesis of 5-amino- and 5-methylthio-4,6-diferrocenyl-1,2,3-



triazines **7a–c**, **8a,b**, and present first data on their reactivity.

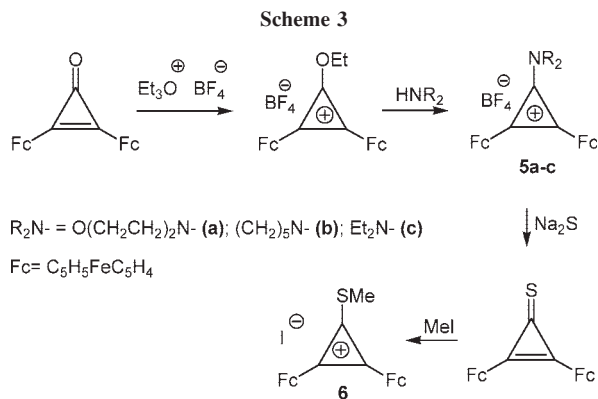
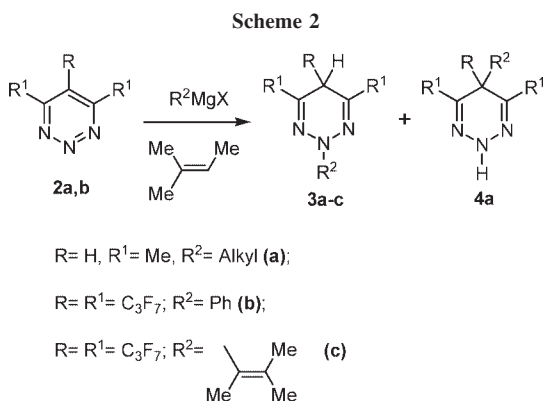
RESULTS AND DISCUSSION

1-Dialkylamino-2,3-diferrocenylcyclopropenylium tetrafluoroborates **5a–c** and 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide **6** obtained as depicted in Scheme 3 [18–20] served as the starting compounds.

Tetrafluoroborates **5a–c** react with sodium azide in dichloromethane, chloroform, acetone, or acetonitrile at ambient temperature (~30 h) or on heating under reflux to give 5-dialkylamino-4,6-diferrocenyl-1,2,3-triazines **7a–c** in ~70–85% yields (Scheme 4). They were obtained as yellow crystalline substances stable on storage in a dry state under ordinary conditions. The structures of compounds **7a–c** were established based on the data from IR spectroscopy, ¹H and ¹³C NMR spectroscopy (which suggest symmetrical structures), and mass spectrometry.

In contrast to tetrafluoroborates **5a–c**, 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide **6** reacted with sodium azide under similar conditions to afford a mixture of isomeric diferrocenyl(methylthio)-1,2,3-triazines **8a** and **8b**. The ratio of the isomers was determined by ¹H NMR spectroscopy, this varied depending on the reaction solvent and temperature (Scheme 5, Table 1).

Separation of the isomers was carried out by chromatography on alumina and characterized by ¹H and ¹³C NMR spectroscopy and mass spectrometry. The data from ¹H and ¹³C NMR spectroscopy suggest symmetrical structure for compound **8a** and nonsymmetrical structure for **8b**.



The structure of one of the reaction products, *viz.*, 4,6-diferrocenyl-5-methylthio-1,2,3-triazine **8a** was confirmed by X-ray diffraction analysis of a single crystal prepared by crystallization from chloroform. The general view of the molecule **8a** and its principal characteristics are given in Figures 1 and 2; the main geometrical parameters are given in Table 2.

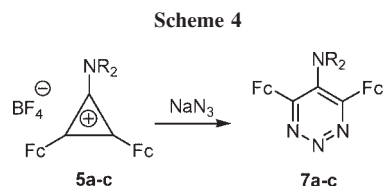
In the molecule of compound **8a**, the substituted cyclopentadienyl rings of the ferrocene fragments are coplanar with, and the ferrocene sandwiches are oriented in opposite directions with respect to, the central planar six-membered ring. The C=N, N=N, Fe–C, and carbon–carbon bonds of the cyclopentadienyl rings as well as the geometrical parameters of the ferrocene sandwiches are close to the standard values [21].

The formation of diferrocenyl-1,2,3-triazines **7a–c** and **8a,b** proceeds apparently with intermediacy of diferrocenylcyclopropenylium azides **9** as ion pairs [1,2,5,9], which undergo reversible transformation to 3-azido(diferrocenyl)cyclopropenes **10a**, **10b**, or **11a,b**, representing allyl azides (Scheme 6).

It is known that allyl azides can undergo [3,3]-sigmatropic rearrangements [22] (Scheme 7).

To all appearance, cyclopropenyl azides **10a**, **10b**, and **11b** transform into 1,2,3-triazine systems according to the mechanism of the [3,3]-sigmatropic rearrangement of allyl azides *via* intermediates **12a**, **12b**, and **13b** (Scheme 8).

None of the presumable intermediates **9**, **10a**, **10b** could be detected even when the reactions were conducted at low temperatures (up to –20°C) in methanol or aqueous methanol. Triazines **7a–c** and **8a,b** were the only reaction products in all cases.



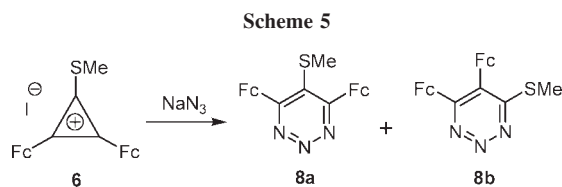


Table 1
Yields of compounds **8a** and **8b**.

Solvent	Temp. (°C)	Time (h)	Yield (%)	
			8a	8b
CH ₂ Cl ₂	20	36	22	56
CH ₂ Cl ₂	35	20	16	68
CHCl ₃	20	30	18	59
CHCl ₃	60	18	15	70
CH ₃ COCH ₃	20	24	19	56
CH ₃ COCH ₃	50	14	17	61
CH ₃ CN	20	25	18	58
CH ₃ CN	60	15	17	58

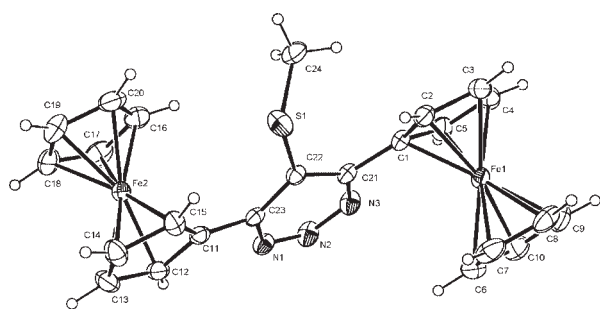


Figure 1. Crystal structure of **8a**.

Different regioselectivity of reactions of 1-amino- and 1-methylthiocyclopropenyl salts with sodium azide is noteworthy. Compounds **5a–c** afforded symmetrical 1,2,3-triazines stereospecifically, whereas compound **6** gave a mixture of 5-methylthio- and 4-methylthio-substituted 1,2,3-triazines **8a** and **8b** in a ratio of ~1:3 or 1:4 with the nonsymmetrical isomer predominating.

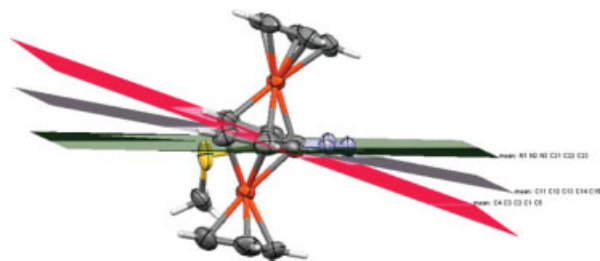


Figure 2. Relative positions of three rings. For plane: C21 C22 C23 N1 N2 N3, maximum deviation from meanplane = -0.136 \AA , with respect plane: C11 C12 C13 C14 C15 and maximum deviation from meanplane = 0.218 \AA , with respect plane: C1 C2 C3 C4 C5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 2
Selected bond lengths and bond angles for **8a**.

Bond lengths, r (Å)		Bond angles, ω (°)	
N(1)-N(2)	1.319(4)	C(23)-N(1)-N(2)	121.1(2)
N(2)-N(3)	1.325(4)	N(1)-N(2)-N(3)	121.2 (2)
N(1)-C(23)	1.355(3)	N(2)-N(3)-C(21)	120.5(2)
C(23)-C(22)	1.405(4)	N(3)-C(21)-C(22)	120.3(3)
C(22)-C(21)	1.399(4)	C(21)-C(22)-C(23)	116.1(2)
C(21)-N(3)	1.349(3)	C(22)-C(23)-N(1)	119.4(3)
C(22)-S(1)	1.773(3)	C(21)-C(22)-S(1)	123.2(2)
C(24)-S(1)	1.799(4)	C(23)-C(22)-S(1)	120.7(2)
C(1)-C(21)	1.479(4)	C(22)-S(1)-C(24)	101.43(14)
C(11)-C(23)	1.470(4)	C(1)-C(21)-N(3)	112.8(2)

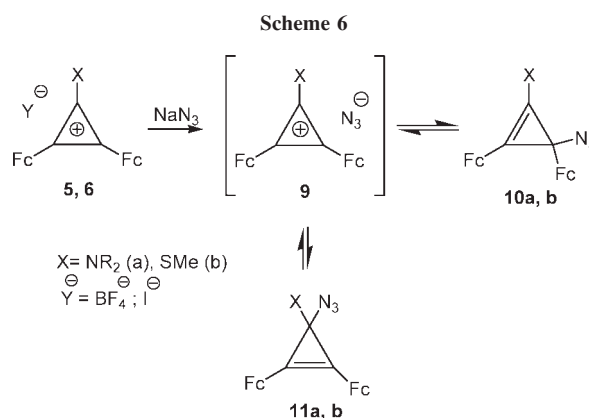
Reactions of triazines **7a–c** with methyl iodide resulted in mixtures of salts **14a–c** and **15a–c** in a ~5:1 ratio (¹H NMR data) (Scheme 9).

Their structures followed from the spectroscopic data (¹H and ¹³C NMR) and confirmed by chemical transformations. Thus, hydrolysis of salts **14a–c** + **15a–c** with an aqueous-ethanolic alkali afforded 4,6-diferrocenyl-2-methyl-1,2,5-dihydro-1,2,3-triazin-5-one **16** and 4,6-diferrocenyl-5-hydroxy-1,2,3-triazine **17** separated by column chromatography on alumina (Scheme 10).

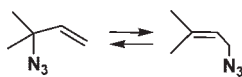
Analogously, triazine **7a** reacts with 1,3-diiodopropane to give salts **18** and **19** (Scheme 11) in a ratio of ~5:1.

Alkaline hydrolysis converted the compound **18** to N(2)-alkylated ketones as about 2:1 mixture of two isomers (*trans*-**20a** and *cis*-**20b**), which could not be separated by chromatography (Scheme 12). However, their identification based on spectroscopic data of ¹H NMR spectra did not present any problems (Table 3). Hydrolysis of the compound **19** affords diketone **21** (Scheme 13).

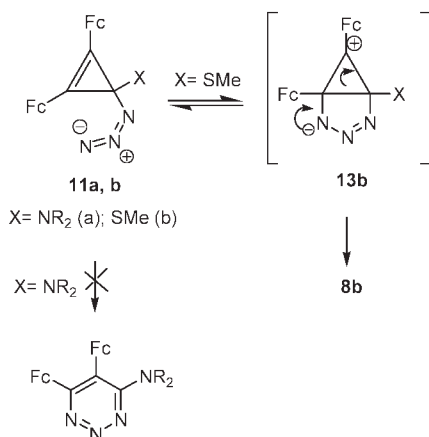
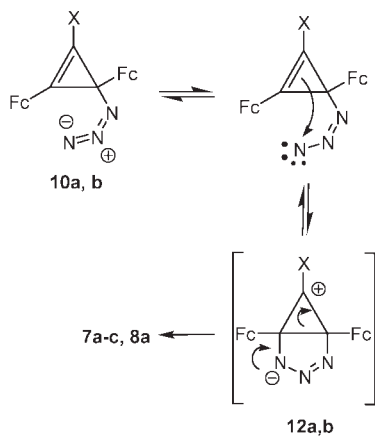
The structures of compounds **18**, **19**, and **21** were confirmed by the data from ¹H and ¹³C NMR



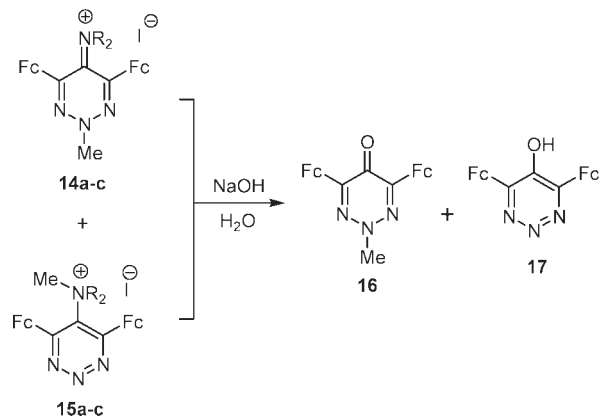
Scheme 7



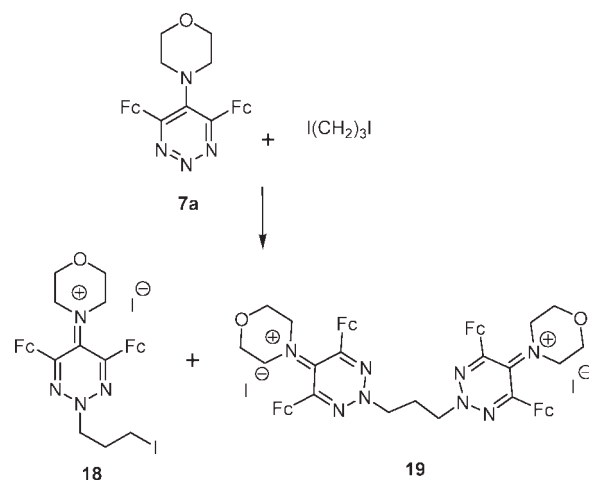
Scheme 8



Scheme 10



Scheme 11

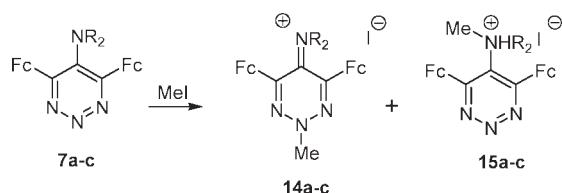


spectroscopy, mass spectrometry, and elemental analysis (Tables 3–5).

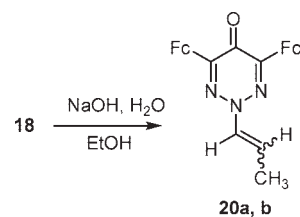
EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in CDCl₃ with Me₄Si as the internal standard. Chemical shifts are given in ppm and *J* values in Hz. The NMR spectroscopic data are listed in Tables 3 and 4.

Scheme 9



Scheme 12



The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). An Elemental Analysis system LECO 1 CHNS-900 was used for determination of elemental analyses (Table 5).

IR spectra of compounds **7a**, **8a**, **8b**, **14a**, **16**, and **20a,b** were obtained for samples as KBr pellets on a Specord IR-75 instrument; UV spectra of compounds **8a**, **8b**, and **16** were recorded on a Specord UV-vis spectrophotometer (Table 6).

Column chromatography was carried out on alumina (Brockmann activity III).

The following reagents were purchased from Aldrich: ferrocene, 98%; aluminum chloride, 99.99%; tetrachlorocyclopropane, 98%; triethyloxonium tetrafluoroborate, 1.0M solution in

Table 3
¹H NMR spectral data of compounds **7a–c**, **8a,b**, **14a–c**, **15a–c**, **16–19**, **20a,b**, **21** (δ /ppm, *J*/Hz).

No.	C ₅ H ₅ (s)	C ₅ H ₄ (m)	CH ₂ (m), CH=, OH (bs)	CH ₃ S (s), CH ₃
7a	4.22 (10H)	4.47 (4H), 4.94 (4H)	2.83 (4H), 3.64 (4H)	–
7b	4.19 (10H)	4.43 (4H), 4.94 (4H)	1.47 (2H), 2.74 (4H), 3.29 (4H)	–
7c	4.13 (10H)	4.48 (4H), 5.06 (4H)	3.00 (q, 4H, <i>J</i> = 7.2)	0.99 (t, 6H, <i>J</i> = 7.2)
8a	4.14 (10H)	4.61 (4H), 5.41 (4H)	–	2.12 (3H)
8b	4.00(5H), 4.15 (5H)	4.33 (2H), 4.40 (2H), 4.48 (2H), 4.51 (2H)	–	2.86 (3H)
14a	4.16 (10H)	4.58 (4H), 4.99 (4H)	3.66 (4H), 3.75 (4H)	4.67 (3H)
14b	4.04 (10H)	4.48 (4H), 4.89 (4H)	1.51 (6H), 3.62 (4H)	4.48 (3H)
14c	4.07 (10H)	4.64 (4H), 5.11 (4H)	3.27 (q, 4H, <i>J</i> = 6.9)	1.12 (t, 6H, <i>J</i> = 6.9), 4.53 (3H)
15a	4.23 (10H)	4.82 (4H), 5.29 (4H)	3.71 (4H), 3.89 (4H)	4.95 (3H)
15b	4.12 (10H)	4.78 (4H), 4.87 (4H)	1.98 (2H), 2.34 (4H), 3.93 (4H)	4.67 (3H)
15c	4.17 (10H)	4.67 (4H), 5.19 (4H)	3.63 (q, 4H, <i>J</i> = 6.6)	1.47 (t, 6H, <i>J</i> = 6.6), 4.68 (3H)
16	4.11 (10H)	4.46 (4H), 5.32 (4H)	–	4.17 (3H)
17	4.09 (10H)	4.49 (4H), 5.27 (4H)	4.52 (1H)	–
18	4.19 (10H)	4.63 (4H), 5.07 (4H)	1.87 (2H), 2.87 (2H), 3.24 (2H), 3.72 (4H), 3.84 (4H)	–
19	4.29 (20H)	4.72 (8H), 5.24 (8H)	3.16 (2H), 3.52 (4H), 3.81 (8H), 3.98 (8H)	–
20a	4.12 (5H), 4.33 (5H)	4.49 (4H), 5.35 (4H)	6.45 (m, 1H, <i>J</i> = 6.9, 14.1), 6.90 (dd, 1H, <i>J</i> = 1.5, 14.1)	1.91 (dd, 3H, <i>J</i> = 1.5, 6.9)
20b	4.10 (5H), 4.13 (5H)	4.39 (4H), 4.65 (4H)	5.50 (m, 1H, <i>J</i> = 7.5, 9.3), 6.81 (dd, 1H, <i>J</i> = 1.8, 9.3)	2.21 (dd, 3H, <i>J</i> = 1.8, 7.5)
21	4.18 (20H)	4.42 (8H), 4.77 (8H)	3.02 (2H), 3.46 (4H)	–

dichloromethane; morpholine, 99+%; sodium hydrosulfide hydrate NaHS·xH₂O; diethylamine, 99.5%; piperidine, 99%; 1,3-diiodopropane, 99%; and sodium azide, 99%.

2,3-Diferrocenylcyclopropenone was obtained from the ferrocene and tetrachlorocyclopropene in the presence of AlCl₃ according to the standard procedure [18]. Ethoxy(diferrocenyl)cyclopropenylium tetrafluoroborate was obtained from the 2,3-diferrocenylcyclopropenone in the presence of triethyloxonium tetrafluoroborate (1.0M solution in dichloromethane) [19]. Amino(diferrocenyl)cyclopropenylium tetrafluoroborates **5a–c** were obtained from ethoxy(diferrocenyl)cyclopropenylium tetrafluoroborate and morpholine, piperidine, or diethylamine in dichloromethane [19,20]. 2,3-Diferrocenylcyclopropenethione was obtained by treating ethanolic diferrocenyl(morpholino)cyclopropenylium tetrafluoroborate with an aqueous solution of NaSH [20], yield 91%, m.p. 208–209°C. 2,3-Diferrocenyl(methylthio)cyclopropenylium iodide **6** was obtained from the 2,3-diferrocenylcyclopropenethione and iodomethane [20]. Freshly prepared and thoroughly dried tetrafluoroborates **5a–c** and iodide **6** were used in the synthesis of 1,2,3-triazines **7a–c** and **8a,b**. Reactions were carried out in freshly distilled dry solvents.

5-Amino-4,6-diferrocenyl-1,2,3-triazines (7a–c). Sodium azide (1.3 g, 20 mmol) was added to a solution of 1-amino-2,3-diferrocenylpropenylium tetrafluoroborate (**5a–c**) (10 mmol) in dichloromethane (chloroform, acetone, or acetonitrile) (100 mL), and the mixture was stirred in a dry inert atmosphere at ~20°C (~24–36 h) or under reflux (14–20 h). The solvents were removed *in vacuo*, and the residues were chromatographed on alumina (hexane–dichloromethane, 4:1) to give 65–78% of triazines **7a–c**.

Reaction of 1-methylthio-2,3-diferrocenylcyclopropenylium iodide 6 with sodium azide. A solution of compound **6** (2.9 g, 5.0 mmol) in a solvent mentioned in Table 1 (100 mL) was stirred with sodium azide (0.65 g, 10 mmol) at ~20°C or with heating for 14–36 h. Subsequent work-up of the reaction mixtures as described earlier gave compounds **8a** and **8b** (see Table 1).

Reactions of triazines 7a–c with methyl iodide. A solution of 5-amino-4,6-diferrocenyl-1,2,3-triazine (**7a–c**) (1.5 mmol) and methyl iodide (3 mL) in dichloromethane (50 mL) was kept at ~20°C for 3 days. The solvent was removed *in vacuo*, and dry benzene (40 mL) was added to the residue. The solids were filtered off and dried to obtain ~75–85% of mixtures of quaternary salts **14a–c** and **15a–c** (~5:1).

Reaction of triazine 7a with 1,3-diiodopropane. The title reaction was carried analogously from 4,6-diferrocenyl-5-morpholino-1,2,3-triazine **7a** (1.6 g, 3 mmol) and 1,3-diiodopropane (0.6 g, 2 mmol) in dichloromethane (50 mL). The violet precipitate that formed was filtered off, washed with dry ether, and dried *in vacuo*. The yield of the diiodide **19** was 0.51 g (25%). The solvent from filtrate was removed *in vacuo*, and

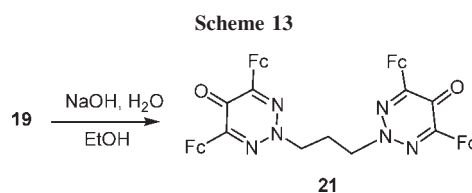


Table 4
¹³C NMR spectral data of compounds **7a–c**, **8a,b**, **14a,b**, **15a**, **16–19**, **21**(δ , ppm).

No.	2 C ₅ H ₅	2 C ₅ H ₄	2 C ₁ ps ₆ Fc	CH ₃	CH ₂ , CH=	C
7a	70.52	69.81, 71.34	81.79	–	49.87 (2), 66.54 (2)	138.64, 156.17 (2)
7b	70.34	69.20, 70.94	81.93	–	23.43, 25.20 (2), 50.87 (2)	139.53, 155.82 (2)
7c	70.29	69.85, 70.77	79.96	13.77 (2)	46.51 (2)	134.80, 159.15 (2)
8a	70.44	71.29, 71.70	78.83	19.0	–	126.11, 161.19(2)
8b	70.21, 70.24	68.97, 69.79, 71.15, 71.52	80.47, 80.52	14.20	–	124.85, 156.48, 162.19
14a	70.73	69.88, 70.86	80.11	51.47	53.15 (2), 65.07 (2)	141.17 (2), 144.10
14b	70.27	68.88, 70.52	79.90	50.22	22.10, 24.92 (2), 53.87 (2)	139.12 (2), 143.61
14c	70.31	68.94, 70.43	80.01	14.67 (2), 51.24	50.28 (2)	140.85 (2), 143.57
15a	70.34	71.14, 72.24	78.57	51.52	53.31 (2), 65.21 (2)	145.20 (2), 147.50
15b	70.21	70.86, 71.56	78.48	50.33	22.34, 25.72 (2), 54.13 (2)	142.31 (2), 146.19
15c	70.27	70.89, 71.83	78.69	14.22 (2), 50.74	49.94(2)	139.97 (2), 142.88
16	69.75	68.97, 69.10, 70.41, 70.51	86.15	50.70	–	152.78 (2), 199.98 (C=O)
17	69.47	68.79, 69.63	80.14	–	–	146.18(2), 153.65
18	70.89	70.97, 71.28	80.43	–	32.41, 36.62, 46.31, 54.22 (2), 65.19 (2)	140.69 (2), 144.34
19	71.03 (2), 71.07 (2)	71.23, 71.31, 71.48, 71.81	80.56, 80.72	–	37.69, 46.82 (2), 55.14 (4), 66.01 (4)	141.53 (2), 143.73 (2), 148.03 (2)
21	70.09 (4)	69.81 (2), 70.64 (2)	87.44 (4)	–	41.53, 49.34 (2)	154.11 (4), 200.04 (2C=O)

Table 5
Yields, mp., elemental analysis, and MS data for the synthesized compounds.

No	Yield (%) (20°C)	Mp. (°C)	Found (%), calculated (%) ^e				Molecular formula	MS, <i>m/z</i> (M ⁺)
			C	H	F	N		
7a	78	244–245	60.85 60–70	5.01 4.91	20.99 20.91	10.39 10.48	C ₂₇ H ₂₆ Fe ₂ N ₄ O	534
7b	74	238–239	63.29 63.19	5.18 5.30	21.12 21.00	10.41 10.52	C ₂₈ H ₂₈ Fe ₂ N ₄	532
7c	81	224–225	62.45 62.34	5.39 5.42	21.59 21.47	10.65 10.77	C ₂₇ H ₂₈ Fe ₂ N ₄	520
8a	18–22	253–254	58.31 58.22	4.19 4.28	22.69 22.56	8.32 8.48	C ₂₄ H ₂₁ Fe ₂ N ₃ S	495
8b	56–59	217–218	58.10 58.22	4.37 4.28	22.43 22.56	8.42 8.48	C ₂₄ H ₂₁ Fe ₂ N ₃ S	495
14a/15a	65/13	272 dec	49.84 49.73	4.40 4.32	16.61 16.52	8.32 8.28	C ₂₈ H ₂₉ Fe ₂ IN ₄ O	676
14b/15b	60/12	235–236	51.79 51.66	4.53 4.64	16.69 16.57	8.21 8.30	C ₂₉ H ₃₁ Fe ₂ IN ₄	674
14c/15c	70/14	224–225	50.65 50.78	4.81 4.72	16.93 16.87	8.31 8.45	C ₂₈ H ₃₁ Fe ₂ IN ₄	662
16	50–62	210–211	60.25 60.16	4.50 4.42	23.17 23.31	8.69 8.77	C ₂₄ H ₂₁ Fe ₂ N ₃ O	479
17	8–11	202–203	59.27 59.40	4.06 4.12	23.89 24.00	9.11 9.03	C ₂₃ H ₁₉ Fe ₂ N ₃ O	465
18	60	270 dec	43.52 43.40	3.92 3.87	13.56 13.45	6.68 6.75	C ₃₀ H ₃₂ Fe ₂ I ₂ N ₄ O	830
19	25	304 dec	50.29 50.17	4.19 4.28	16.58 16.37	8.12 8.21	C ₅₇ H ₅₈ Fe ₄ I ₂ N ₈ O ₂	–
20a,b	71	164–165	61.77 61.82	4.48 4.59	22.23 22.11	8.25 8.32	C ₂₆ H ₂₃ Fe ₂ N ₃ O	505
21	69	321–322	60.75 60.66	4.29 4.36	23.17 23.03	8.58 8.66	C ₄₉ H ₄₂ Fe ₄ N ₆ O ₂	970

Table 6
IR and UV spectral data of compounds **7a**, **8a**, **8b**,
14a, **16**, and **20a,b**.

No.	ν_{\max} (KBr)/ cm^{-1}	$\lambda_{\max}(\text{CHCl}_3, 20^\circ)/\text{nm}$
7a	435, 488, 544, 594, 736, 821, 887, 910, 943, 1001, 1021, 1039, 1067, 1108, 1186, 1261, 1384, 1443, 1509, 1636, 2851, 2897, 2959, 3090, 3440	–
8a	416,482, 503, 548, 674, 750, 786, 824, 890, 1000, 1015, 1064, 1106, 1178, 1237, 1289, 1304,1388, 1408, 1434, 1487, 1503, 1636, 2921, 2994, 3090, 3439	242, 288.15, 492.50
8b	415, 482, 502, 548, 733, 749, 785, 829, 999, 1024, 1068, 1105, 1119, 1177, 1234, 1289, 1306, 1389, 1410, 1438, 1499, 1639, 1670, 2921, 3089, 3428	210, 245, 290
14a/15a	498, 524, 617, 708, 736, 822, 916, 1001, 1028, 1061, 1107, 1240, 1268, 1306, 1356, 1400, 1434, 1483, 1549, 1627, 1703, 2859, 2956, 3048, 3420	–
14b/15b	493, 518, 613, 701, 740, 818, 922, 1003, 1021, 1060, 1106, 1243, 1274, 1332, 1420, 1439, 1482, 1551, 1628, 1708, 2861, 2934, 3042, 3417	–
14c/15c	496, 521, 619, 711, 735, 819, 913, 1002, 1026, 1068, 1103, 1241, 1272, 1337, 1421, 1432, 1478, 1557, 1631, 1704, 2861, 2929, 3046, 3423	–
16	495, 543, 590, 662, 724, 816, 916, 1001, 1023, 1066, 1205, 1292, 1324, 1379,1408, 1438, 1470, 1494, 1595, 1609, 1640, 1692, 2866, 2948, 3089, 3429	210.38, 278.50, 307.50, 346.40
20a,b	427, 465, 479, 553, 724, 818, 843, 912, 1003, 1029, 1050, 1107, 1155, 1230, 1325, 1378, 1411, 1440, 1470, 1494, 1597, 1612, 1643, 1666, 2864, 2971, 3093, 3452	–

dry ether (100 mL) was added to the residue. The solid was filtered off, dried to obtain 1.46 g (60%) of iodide **18**.

Alkaline hydrolysis of salts (14a–c + 15a–c), 18, and 19. A mixture of quaternary salts (**14a + 15a**), (**14b + 15b**), (**14c + 15c**), (**18**), or (**19**) (1 mmol) in 10% aqueous NaOH (5 mL) and ethanol (50 mL) was stirred under reflux for 4 h. On cooling, water (100 mL) and chloroform (50 mL) were added, the reaction mixtures were stirred for additional 10 min, the organic layer was separated and concentrated *in vacuo*. The residues were chromatographed on alumina (hexane–dichloromethane, 5:1) to yield 2,5-dihydro-1,2,3-triazine-5-on and 5-ol **16** and **17**, compounds **20** and **21**.

Determination of the crystal structure. The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4 diffractometer. The structure of compound **8a** was solved by the direct method (SHELXS -97 [23]) and refined using full-matrix least-squares on F^2 .

Crystal data for $\text{C}_{24}\text{H}_{21}\text{Fe}_2\text{N}_3\text{S}$ (**8a**): $M = 495.20 \text{ g mol}^{-1}$, monoclinic $P2_1/c$, $a = 7.8403(12)$, $b = 16.025(3)$, $c = 16.655(3) \text{ \AA}$, $\alpha = 90$, $\beta = 99.300(11)$, $\gamma = 90^\circ$, $V = 2065.1(6) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $Z = 4$, $\rho = 1.593 \text{ Mg/m}^3$, $\lambda (\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, $F(000) = 1016$, absorption coefficient 1.522

mm^{-1} , index ranges $-1 \leq h \leq 9$, $-1 \leq k \leq 19$, $-20 \leq l \leq 20$, scan range $2.48 \leq \theta \leq 25.98^\circ$, 4046 independent reflections, $R_{\text{int}} = 0.0395$, 5339 total reflections, 272 refinable parameters, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0346$, $wR_2 = 0.0759$, R indices (all data) $R_1 = 0.0513$, $wR_2 = 0.0837$, largest difference peak and hole 0.330/–0.359 e-\AA^{-3} .

CCDC-676457 (for **8a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html.

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