the end point was not distinct. The products were stored (frozen) in serum bottles under argon.

Preparation of 3-Aryl-5,5-dimethylthiazolidine-2-thiones (6a–c). The general method[5] was to reflux a mixture of the thiol (3.0 mmol) or disulfide (1.5 mmol), 10 *N* NaOH (0.30 ml), CS_2 (7 mmol), and ethanol (10 ml) for 24 hr (argon), add water (3–4 ml), and chill. The crystalline derivative was filtered, washed (cold MeOH, then H_2O), and recrystallized from the same ethanol–water mixture prior to analysis. The yields listed are for the crude products. Use of the disulfides **3a** and **3c** led to similar (or higher) yields of the identical **6** (melting point and mixture melting point).

3-Phenyl-5,5-dimethylthiazolidine-2-thione (6a): colorless plates (45%), mp 114–115°. Anal. Calcd for $C_{11}H_{13}NS_2$: C, 59.15; H, 5.86; N, 6.27. Found: C, 58.80; H, 5.87; N, 6.17.

3-(*p*-Chlorophenyl)-5,5-dimethylthiazolidine-2-thione (6b): colorless needles (34%), mp 111–111.5°. Anal. Calcd for $C_{11}H_{12}ClNS_2$: C, 51.25; H, 4.69; N, 5.43. Found: C, 51.34; H, 4.81; N, 5.81.

3-(*p*-Dimethylaminophenyl)-5,5-dimethylthiazolidine-2-thione (6c): pale yellow needles (79%), mp 156–157° (lit.[5] 157–158°).

Nickel(II) Complex of 5. A solution of **5** (1 mmol) in MeOH (4 ml) was added to a warm solution of $Ni(OAc)_2 \cdot 4H_2O$ (1 mmol) in MeOH (8 ml). The solid, which separated immediately, was filtered, washed (MeOH), and vacuum dried (1 hr at 50°) to give 188 mg (61.4%) of the tan-pink crystalline complex. Its ir spectrum exhibited bands at 3220 and 3270 cm^{-1} (sh) (coordinated NH). Anal. Calcd for $C_{10}H_{22}N_2S_2Ni \cdot \frac{1}{2}H_2O$: C, 39.75; H, 7.67; N, 9.27. Found: C, 39.67; H, 7.85; N, 9.59.

Registry No.—**1a,** 54410-19-4; **1b,** 54410-20-7; **1c,** 54410-23-0; **1d,** 57443-08-0; **2a,** 54410-26-3; **2b,** 54410-28-5; **2c,** 54410-33-2; **2d,** 54410-35-4; **3a,** 57443-09-1; **3b,** 57443-10-4; **3c,** 57443-11-5; **3d,** 57443-12-6; **4,** 57443-13-7; **5,** 57443-14-8; **5** Ni(II) complex, 57443-07-9; **6a,** 57443-15-9; **6b,** 57443-16-0; **6c,** 54410-36-5; α,α′-dithiodiisobutyraldehyde, 15581-80-3; aniline, 62-53-3; *p*-chloroaniline, 106-47-8; *N,N*-dimethyl-*p*-phenylenediamine, 99-98-5; methylamine, 74-89-5; $Ni(OAc)_2$, 373-02-4.

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Ferrocene-1,1′-disulfonyl Azide and 2,4,6-Trimethylpyridinium Ferrocenesulfonyl Ylide. Synthesis and Decomposition

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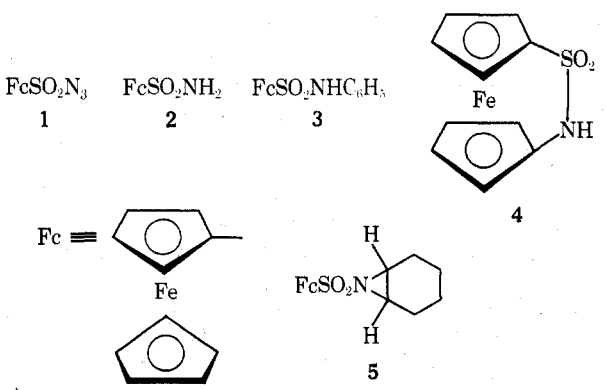
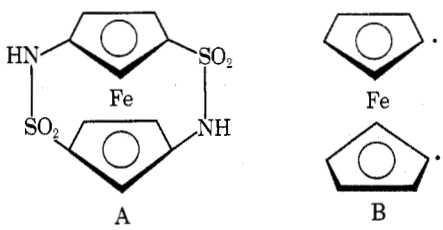
Photolysis of ferrocene-1,1′-disulfonyl azide in various solvents and at different wavelengths gave 1′-sulfamylferrocenesulfonyl azide and ferrocene-1,1′-disulfonamide. The thermolysis products depended on the solvent used. In cyclohexane, 1′-sulfamylferrocenesulfonyl azide, ferrocene-1,1′-disulfonyl azide, *N,N′*-dicyclohexylferrocene-1,1′-disulfonamide, 1′-(*N*-cyclohexylsulfamyl)ferrocenesulfonyl azide, and 1′-(*N*-cyclohexylsulfamyl)ferrocenesulfonamide were obtained. In benzene, products both of kinetic (azepine) and thermodynamic control (anilide) were formed but disubstitution did not occur. In mesitylene, the dimesitylamide was obtained. No intramolecular cyclization products were ever detected. 2,4,6-Trimethylpyridinium ferrocenesulfonyl ylide did not undergo photolysis but did thermolyze to ferrocenesulfonamide and *sym*-collidine. Again no ferrocenophane was formed.

The thermal and photochemical decomposition of ferrocenylsulfonyl azide (**1**) has led to some very interesting results.[1,2] Thermolysis in benzene led to a unusually high yield (for such reactions[3]) of hydrogen-abstraction product, ferrocenesulfonamide (**2**), and to a low yield of "substitution"[4] into the aromatic nucleus (**3**).[2] More solvent insertion and less hydrogen abstraction were observed in cyclohexane, but the yield of **2** was very high in cyclohexene. Photolysis of **1** led to quite different results. Thus, the main product formed in benzene was the novel bridged derivative **4**, [2]ferrocenophanethiazine 1,1-dioxide,[1] together with much smaller amounts of **2**. The same products were formed in cyclohexene, but now, for the first time, was observed what is probably the addition of a singlet sulfonyl

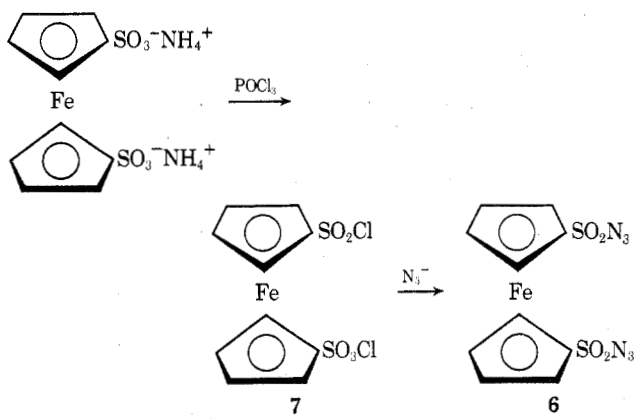


nitrene to an olefinic double bond, namely the aziridine derivative **5**.[2]

In a subsequent study, the decomposition of *o*- and *p*-benzenedisulfonyl azides in various solvents was examined.[5] A number of interesting reactions were observed, particularly with the ortho derivative, decomposition of which led, among others, to the generation of benzyne, as well as to the loss of one of the sulfonyl azide moieties. It was, therefore, decided to study the behavior of ferrocene-1,1′-disulfonyl azide (**6**). Among the possibilities were that a ferrocenophane derivative related to **4** would be formed and that the second sulfonyl azide group would react with solvent [formation of a dibridged species such as A was considered unlikely since models showed (and x-ray analysis has since confirmed[6]) that the two cyclopentadienyl rings were certainly not parallel in **4**]. As well, the formation of a "ferrocyne" (B) was a possibility. Certainly, it was felt that interaction between the two sulfonyl azides functions was possible and that this would result in some interesting behavior, and this is what has been observed. No evidence for the formation of A or B has been found.



Ferrocene-1,1′-disulfonyl azide (**6**) was prepared from diammonium ferrocene-1,1′-disulfonate (**9**)[7] with phosphorus oxychloride (no product was obtained with phosphorus trichloride), followed by treatment of **9** with sodium azide in aqueous acetone. It was found necessary to protect the azide from light during the reaction and after isolation, since the compound darkened noticeably on exposure to ordinary light. The structure of the diazide was confirmed by its spectroscopic properties: ν_{max} 2155 (N_3), 1355 and 1150 cm^{-1} (SO_2), two triplets of equal intensity centered at δ 4.83 (β-H) and 5.00 (α-H) (A_2B_2), and $M^{\cdot+}$ *m/e* 396.

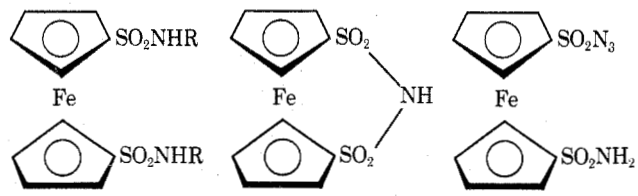


An authentic sample of *N,N′*-dicyclohexylferrocene-1,1′-disulfonamide (**8**) (an expected product from one of the reactions) was readily prepared from **7** and cyclohexylamine, but ferrocene-1,1′-disulfonamide (**9**) could not be obtained from **7** and ammonia under a large variety of conditions and solvents, e.g., aqueous or dry ammonia in benzene, ethyl acetate, or acetone. Since only small amounts of **7** were recovered we suspect that a bridged imide such as **10** may form which decomposes readily to give dark, intractable products. Amides **9** and **11** obtained as described below appear to be stable. Similar results were obtained on attempted preparation of **11** from **7** and aniline.

Table I
Photolysis of Ferrocene-1,1′-disulfonyl Azide (6) at 35°

Solvent	Wavelength, Å	Time, hr	Recovered 6, %	% 9	% 12
C_6H_6	2537	1	62.3		17
C_6H_6	3000	1	14.2		25
C_6H_6	3500	1	50.0		11
C_6H_6	3500	8	5.3	3.6	5.1
C_6H_6[a]	3000	1	70.6		22
C_6H_{12}	2537	1	54.7		9
C_6H_{12}	3000	1	78.4		17
C_6H_{12}	3500	1	56.5		16
C_6H_{10}	3000	1	76		21

[a] Ferrocene added as sensitizer; 92% was recovered.



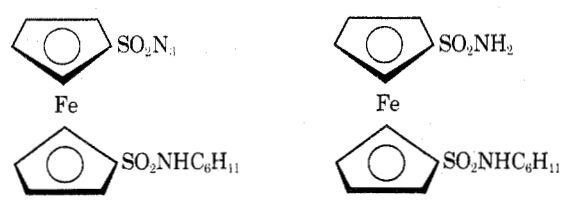
8, R = C_6H_{11}
9, R = H
11, R = Ph

10 **12**

Photolysis of **6** in benzene, cyclohexane, or cyclohexene at various wavelengths and for varying periods of time gave only two identifiable products and a lot of insoluble tarry material. The results are summarized in Table I. The first of these products was identified as 1′-sulfamylferrocenesulfonyl azide (**12**) on the basis of its spectral properties: ν_{max} 3280, 3210 (NH_2), 2120 (N_3), 1375, 1320, and 1135 cm^{-1} (two different SO_2); two A_2B_2 systems, δ 4.95 (H_2, H_5), 4.81 (H_3, H_4), 4.95 (H_2', H_5', overlapping with H_2 and H_5), 4.68 (H_3', H_5'). The base peak in the mass spectrum of **12** was at *m/e* 344, which corresponds to $M^{\cdot+} - 26$. This could either be due to loss of N_2 followed by hydrogen abstraction to give the **9** ion (indeed, with the exception of a small peak corresponding to $M^{\cdot+} - 28$, the rest of the spectrum was the same as that of **9**), or to the loss of C_2H_2 as has been found to be the case with some aryl azides.[8] If **9** was indeed formed it would probably have to be in the inlet of the mass spectrometer by thermolysis and intramolecular hydrogen abstraction prior to volatilization. This remains to be resolved by accurate mass measurements. Continued photolysis of **12** did not lead to any ferrocenophane formation.

The second product formed in the photolyses on longer irradiation was ferrocene-1,1′-disulfonamide (**9**). It exhibited bands at 3330, 3255 (NH_2), 1345, and 1145 cm^{-1} (SO_2), an A_2B_2 system [δ 4.85 (4, α-H), 4.65 (4, β-H), 7.15 (4, exchangeable NH_2)], and a parent ion (also the base peak) at *m/e* 344. It is likely that **9** is formed from **12** on longer exposures (Table I).

Thermolysis of **6** in cyclohexane at 135° for 16 hr gave **9** (7.8%), **8** (8.7%), 1′-(cyclohexylsulfamyl)ferrocenesulfonyl azide (**13**, 0.6%), and 1′-(*N*-cyclohexylsulfamyl)ferrocenesulfonamide (**14**, 10.7%). When the thermolysis was carried out for only 4 hr, only **13** (26.2%) and **12** (4.7%) were



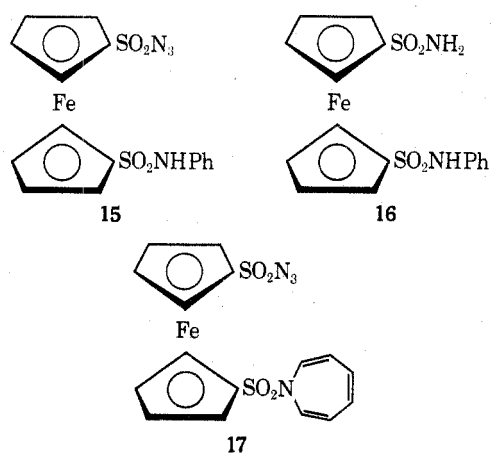
13 **14**

Table II
Thermolysis of 6 in Benzene

Temp, °C	Time, hr	Additives	Products, % Recovered 6	9	12	15	17	Other
135	4		23	trace	8.2	12.5		
135	16			5.4				Aniline (trace)
135	3	Ferrocene	14		16.2	15.1		Ferrocene (94.5)
135	3	Tetracyclone	16.1	14.4	12.3	8.5		Tetracyclone (88.6)
135	4	TCNE	8	3.1	6.4	2.4		
100	63		54	1.4	8.2	6.3	9.4	
100	116		18.5	2.4	5.2	2.8	2.5	
100	188		13.9	6.8	4.6	3.9	0.5	
100	53	TCNE	71	2.8	5.0	3.0		

obtained, and much azide (43%) was recovered. The structural assignments of **13** and **14** are based on the spectroscopic properties of the compounds (see Experimental Section). It seems likely, therefore, that **9** arises from **12** in this reaction on prolonged heating, while **14** arises from **13** by hydrogen abstraction by the sulfonyl nitrene from the solvent. When the thermolysis was carried out at 100° for 53 hr, **13** (9%), **12** (2.7%), and **9** (7.2%) were obtained, together with much recovered azide (34.4%).

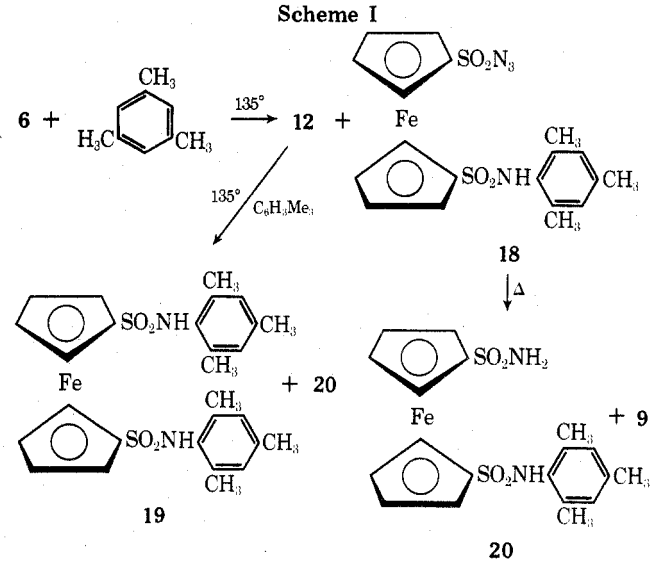
The results of the decomposition of **6** in benzene are given in Table II. At 135°, 1′-(*N*-phenylsulfamyl)ferrocenesulfonyl azide (**15**) was obtained. Interestingly neither the disulfonanilide (**11**) nor 1′-(*N*-phenylsulfamyl)ferrocenesulfonamide (**16**) could be detected, though a careful



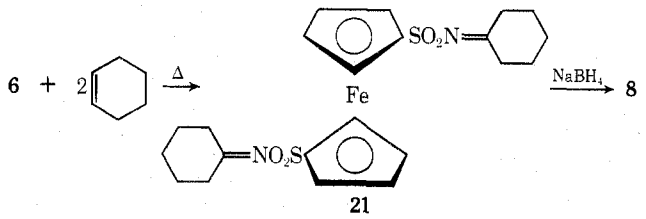
search was made for them. This contrasts (as do most of the above results) with the behavior of *o*-benzenedisulfonyl azide, which, on thermolysis in benzene, gives both *o*-benzenedisulfonylanilide and benzenesulfonylanilide-2-sulfonamide.[5] The addition of ferrocene to the solution before thermolysis had a slight beneficial effect upon the yields of products but no change in their nature was observed. When the temperature at which the thermolysis was carried out was lowered a new product was obtained which proved to be the *N*-sulfonylazepine **17**. Evidence of its structure is based mainly on the infrared, NMR, and mass spectra of **17**, since, unlike simpler *N*-acylazepines,[9,10] no [4 + 2]π adduct was formed with tetracyanoethylene (TCNE) nor could the azepine be trapped with tetracyclone (which gives [4 + 2]π and [6 + 4]π adducts with *N*-mesylazepine[11]). It exhibited bands at 2130 (N_3), 1640, 1620 (C=C in azepine[12]), 1360, and 1145 cm^{-1} (SO_2), the usual 1,1′-disubstituted ferrocene A_2B_2–$A_2'B_2'$ patterns in the NMR, as well as a complex multiplet (6 H) at δ 5.96 and 5.67 (azepine vinyl protons[12]). The base peak in the mass spectrum was at *m/e* 92 corresponding to $C_6H_6N^+$, the azatropylium ion, behavior characteristic of N-substituted azepines.[12] *N*-Mesylazepine has previously been isolated from the decomposition of $MeSO_2N_3$ in benzene at 80–100° and is the product of kinetic control.[9] At higher temperatures, the *N*-sulfonylanilide is formed (in the present case, **15**) as the product of thermodynamic control.

In the hope of achieving attack by *both* sulfonylnitrene groups upon the solvent aromatic nucleus, the latter was made more nucleophilic and the thermolysis of **6** in mesitylene was examined. At 135° for 3 hr the only products formed were **12** (13.5%) and 1′-(*N*-2,4,6-trimethylphenylsulfamyl)ferrocenylsulfonyl azide (**18**, 26.2%). Starting azide was recovered. When heating was prolonged for 16 hr, however, *N,N′*-di-(2,4,6-trimethylphenyl)ferrocene-1,1′-disulfonamide (**19**, 11.6%) *was* obtained, together with 1′-(*N*-2,4,6-trimethylphenylsulfamyl)ferrocenesulfonamide (**20**, 17.2%) and **9** (14.2%). These products probably arise as shown in Scheme I.

Scheme I



Decomposition of **6** in boiling cyclohexene give the diimine **21** (no NH absorption; strong band due to C=N at 1610 cm^{-1}) which was very unstable and hydrolyzed very readily in moist air to give cyclohexanone and **9** (65%). Reduction of the reaction product with $NaBH_4$ without isolation gave **8** (42.6%), together with some **9** (24.3%) undoubtedly due to hydrolysis of **21** before addition of borohydride. The reaction of sulfonyl azides with unstrained olefins has been reported[13,14] to give imines, probably by 1,3-dipolar addition of the azide to the olefin followed by thermal elim-

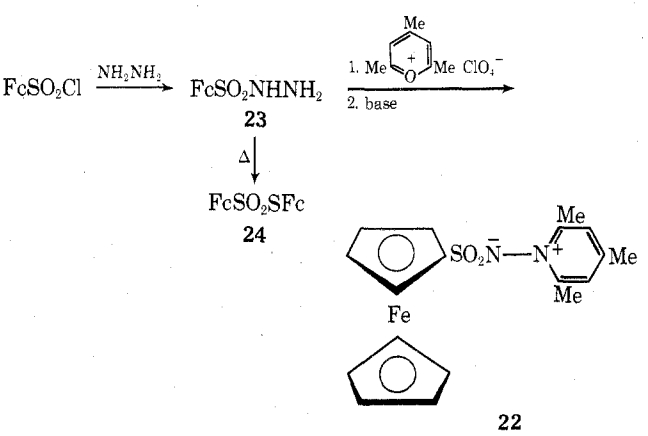


ination of N_2, and the in situ reduction of the imines to sulfonamides with $NaBH_4$ has been described.[14]

Even when an "inert" solvent not containing hydrogen was used, hydrogen abstraction products were the only ones that could be isolated in low yield: no intramolecular cyclization was achieved with the disulfonyl azide. Thus, thermolysis of **6** in Freon 113 gave only **9** (3.5%) and **12** (2.8%), so that intermolecular hydrogen abstraction, or hydrolysis of more complex materials during work-up, must be occurring.

It was of interest to see whether the ferrocenophane **4** could be obtained from a source other than the sulfonyl azide. To that end, 2,4,6-trimethylpyridinium ferrocenesulfonyl ylide (**22**) was prepared by the sequence in Scheme II.

Scheme II



Ylide **22** appears to fragment in a number of ways upon electron impact. The most important pathway seems to be fragmentation to the collidinium radical cation *m/e* 121 (100) and ferrocenesulfonylnitrene, the latter undergoing a Curtius-type rearrangement with loss of SO_2 to give ferrocenylnitrene [*m/e* 199 (12)].[15] Other important fragments are $Me_3C_5H_2N^+$–N [*m/e* 135 (21%)][15] and $FcSO_2NH_2^+$ [*m/e* 265 (36)]. Contrary to the behavior of *N*-methanesulfonylimino-2,4,6-pyridinium ylide, which gives a diazepine on photolysis,[15] irradiation of **22** with 2500-, 3000-, or 3500-Å light led only to the recovery of the ylide. Thermolysis of **22** in benzene at 175° gave $FcSO_2NH_2$ (54%) and 2,4,6-collidine (71%). No intramolecular cyclization to **4** was observed in accord with the fact that no singlet sulfonylnitrenes have been observed in the photolysis of *N*-sulfonyliminopyridinium ylides[15] and the suggestion that thermal decomposition of ferrocenesulfonyl azide leads to a nitrene metal complex which hydrogen abstracts rather than cyclizes.[2]

It was noted that ferrocensulfonyl hydrazide (**23**) melted with evolution of a gas and then resolidified. This sequence was carried out on a preparative scale at 150–160°. A basic gas was evolved and the yellow residue was shown to be ferrocenyl ferrocenethiolsulfonate (**24**). Small amounts of ferrocene were also formed in this reaction.

Experimental Section

Melting points are uncorrected. Ir spectra were determined on Perkin-Elmer 257, 357, or Beckman Acculab 3 instruments, and NMR spectra on a Varian Associates HA-100 or a Hitachi Perkin-Elmer R20B spectrometer using tetramethylsilane as internal standard. The mass spectra were determined on a CEC 21-104 or Hitachi Perkin-Elmer RMU-6M spectrometer and uv spectra on a Cary 14 spectrophotometer.

Reagents and solvents were usually reagent grade and were fractionally distilled or recrystallized before use. Drying of organic extracts was effected with calcium chloride, magnesium sulfate, or molecular sieves (Davidson, type 4A, grade 514, 8–12 mesh). Light petroleum refers to the fraction of bp 30–60° unless otherwise stated. Basic alumina for chromatography was Alcoa (F-20) and neutral alumina was prepared from this basic alumina.

Ferrocene-1,1′-disulfonyl Azide (6). A stirred mixture of phosphorus oxychloride (50 ml) and diammonium ferrocene-1,1′-disulfonate (16.5 g) was heated under reflux on a steam bath for 6 hr. The yellow salt had turned to a white solid. The slurry was cooled, ice water (50 ml) was added carefully, and the solution was poured onto ice (400 g). A dark precipitate was collected, dried in vacuo, dissolved in chloroform (400 ml), and filtered to remove a rust-colored insoluble material. Light petroleum (400 ml) was added, and the solution was treated with charcoal and cooled in a dry ice–acetone bath. Yellow-orange crystals were collected, washed with light petroleum (2 × 20 ml), and dried in vacuo to give ferrocene-1,1′-disulfonyl chloride (10.6 g, 62%) which had no clear melting point but darkened noticeably at 160° and was black by 180°: ir (KBr) 1360 (s), 1205 cm^{-1} (s); NMR ($CDCl_3$) δ 4.80 (t, 2 H), 5.02 (t, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 386 ($M^{\cdot+}$ $^{37}Cl_2$, 4), 384 (16), 382 (23).

The chloride (10.5 g) in acetone (300 ml) was treated dropwise with sodium azide (4.1 g) in water (50 ml) with vigorous stirring at room temperature for 24 hr in the absence of light, evaporated to about 40 ml in vacuo, and poured into water. The yellow precipitate was collected, washed with water (3 × 30 ml), and dried under vacuum. It was recrystallized from absolute ethanol to give yellow prisms of **ferrocene-1,1′-disulfonyl azide** (6.1 g, 58%): mp 128–129° dec; λ_{max} (EtOH) 207, 247, and 307 nm (ε 34 200, 10 810, and 2250).

Anal. Calcd for $C_{10}H_8FeN_6O_4S_2$: C, 30.32; H, 2.04. Found: C, 30.56; H, 2.16.

***N,N′*-Dicyclohexylferrocene-1,1′-disulfonamide (8).** Ferrocene-1,1′-disulfonyl chloride (3.76 g) was dissolved in benzene (50 ml) and cyclohexylamine (6.2 g) was added dropwise. The solution was boiled under reflux for 12 hr in the absence of light. It was then evaporated under vacuum, the dark, oily material was poured into 3 *N* HCl (100 ml), and the dark precipitate was collected and dried in vacuo (3.62 g). Recrystallization from light petroleum (bp 60–110°)–ethyl acetate gave ***N,N′*-dicyclohexylferrocene-1,1′-disulfonamide (8,** 1.88 g, 36%): mp 203–204° dec; ir (KBr) 3310 and 3270 (s, br), 1320 (s), 1190 (s), 1135 cm^{-1} (s); NMR ($CDCl_3$) δ 4.81 (t, 4 H), 4.61 (t, 4 H), 4.49 (s, exchanges with D_2O), 3.12 (s, br, 2 H), and 1.0–0.9 (br, 20 H); mass spectrum (70 eV) *m/e* (rel intensity) 510 (14), 509 (30), 508 ($M^{\cdot+}$, 100).

Anal. Calcd for $C_{22}H_{32}FeN_2O_4S_2$: C, 51.97; H, 6.34. Found: C, 52.23; H, 6.54.

Attempted Preparation of Ferrocene-1,1′-disulfonamide. Ferrocene-1,1′-disulfonyl chloride (2.15 g) was dissolved in acetone (40 ml) and 15 *M* aqueous ammonia (30 ml) was added. The solution was boiled under reflux for 1 hr on a steam bath and cooled, a second portion of aqueous ammonia (20 ml) was added, and the solution was boiled under reflux for another 1 hr. It was evaporated under vacuum to ca. one-third of its volume and poured into water (200 ml). A dark solid was collected, dried, and dissolved in ethyl acetate, dried ($CaCl_2$), and evaporated onto neutral alumina (ca. 20 g). Chromatography on a column of neutral alumina (2.3 × 35 cm) yielded only starting disulfonyl chloride (0.12 g, 6%) which eluted with benzene–ethyl acetate (1:1 v/v).

Similar reactions using benzene as solvent and 15 *M* aqueous ammonia gave only small quantities of starting disulfonyl chloride.

Ferrocene-1,1′-disulfonyl chloride (1.50 g) was dissolved in benzene (80 ml, Na dried) and ammonia gas (KOH dried) was bubbled through the solution for 2 hr at room temperature. A dark precipitate formed continuously during the addition. This solution, including the precipitate, was evaporated in vacuo onto neutral alumina (ca. 20 g) and chromatographed as above. Only ferrocene-1,1′-disulfonyl chloride (0.025 g, 17%) was obtained. Similar reactions carried out in acetone, ethyl acetate, and chloroform gave only small amounts of recovered disulfonyl chloride.

Attempted Preparation of *N,N′*-Diphenylferrocene-1,1′-disulfonamide. Ferrocene-1,1′-disulfonyl chloride (1.82 g) was dissolved in acetone (30 ml) and aniline (8.0 g) was added. The solution was boiled under reflux for 12 hr in the absence of light. It

was cooled and concentrated under vacuum, the dark, oily residue was poured into 3 *N* HCl (100 ml), and the acid solution was extracted with ether (3 × 50 ml). The ether solution was dried ($CaCl_2$) and evaporated under vacuum into neutral alumina (ca. 20 g). Chromatography on a column of neutral alumina (2.3 × 40 cm) yielded only starting disulfonyl chloride (0.35 g, 19%).

Reaction of 1,1′-ferrocenedisulfonyl chloride with aniline in benzene in the presence of an excess of triethylamine at room temperature for 14 days yielded only a small amount of starting disulfonyl chloride.

Photolysis of Ferrocene-1,1′-disulfonyl Azide in Benzene Using 2537-Å Radiation for 1 Hr. The azide (0.74 g) was dissolved in benzene (100 ml, Na dried) and nitrogen (dry, O_2 free) was bubbled through the solution for 30 min. It was then irradiated in a Vicor vessel fitted with a Pyrex glass wool stirrer to clean the sides of the vessel in a Rayonet reactor equipped with 2537-Å lamps for 1 hr at 35° under dry, oxygen-free nitrogen. After irradiation the solution was pale yellow with a brown solid material adhering to the glass wool. The solution was removed, the apparatus washed with ethyl acetate (3 × 20 ml), the glass wool extracted with ethyl acetate (3 × 40 ml) until colorless, and the combined solutions evaporated in vacuo onto neutral alumina (10 g). Chromatography on a column of neutral alumina (2.3 × 25 cm) and elution with benzene–ethanol (99.5:0.5 v/v) and benzene–ethanol (98:2 v/v) gave starting azide (0.46 g, 62.3%) (infrared spectrum identical with that of authentic azide). Elution with benzene–ethanol (96:4 v/v) gave **1′-sulfamylferrocenesulfonyl azide (12,** 0.045 g, 17%) (from ethyl acetate–light petroleum), mp 154–156° dec.

Anal. Calcd for $C_{10}H_{10}FeN_4O_4S_2$: C, 32.45; H, 2.72. Found: C, 32.73; H, 2.81. No other compounds were eluted.

The azide **6** was photolyzed under identical conditions but using 3000 Å and 3500 Å. The results are given in Table I.

Photolysis of 6 in Benzene for 8 Hr. The azide (1.47 g) in benzene (100 ml, Na dried) in a Pyrex vessel was irradiated using 3500-Å lamps for 8 hr at ca. 35°. The photolysis mixture was chromatographed as above. Elution with benzene–ethyl acetate (99:1 v/v) gave starting azide (0.079 g, 5.3%). Elution with ethyl acetate–ethanol (99:1 v/v) gave 1′-sulfamylferrocenesulfonyl azide (0.067 g, 5.1%) (ir spectrum identical with that of compound obtained above). Elution with ethyl acetate–ethanol (99:1 and 95:5 v/v) gave yellow, granular crystals of **ferrocene-1,1′-disulfonamide (9,** 0.045 g, 3.6%), darkens at 180°, mp 198–202° dec (from ethyl acetate–light petroleum).

Anal. Calcd for $C_{10}H_{12}FeN_2O_4S_2$: C, 34.90; H, 3.55. Found: C, 35.12; H, 3.40.

No other compounds were eluted.

Photolysis at 3000 Å of 6 in Benzene in the Presence of Ferrocene. The azide (0.84 g) and ferrocene (4.88 g) were dissolved in benzene (100 ml, Na dried) and the solution was photolyzed using 3000-Å lamps for 1 hr at 30°. The photolysis mixture was chromatographed as above. Elution with benzene gave ferrocene (4.52 g, 92%). Further elution with benzene gave starting azide (0.59 g, 70.6%). Elution with benzene–ethanol (9:1 v/v) gave 1′-sulfamylferrocenesulfonyl azide (0.049 g, 22%) (ir spectrum identical with that of product obtained above).

Photolysis of 6 in Cyclohexane Using 2537-Å Radiation. The azide (0.69 g) was added to cyclohexane (100 ml, Na dried) and the solution flushed with nitrogen (dry, O_2 free) for 30 min. Not all of the azide was dissolved at this time. The suspension was irradiated for 1 hr at ca. 30° using 2537-Å lamps. The product was isolated and chromatographed as above. Elution with benzene–ethyl acetate (99:1 v/v) gave starting azide (0.38 g, 54.7%). Elution with benzene–ethanol (98:2 v/v) gave 1′-sulfamylferrocenesulfonyl azide (0.026 g, 9%).

The results of related reactions at other wavelengths and in cyclohexene are collected in Table I.

General Procedure for the Thermal Decompositions. The azide was added to the solvent in a thick-walled glass vessel containing a small glass rod. Nitrogen (dry, O_2 free) was flushed through the solution for 30 min and the vessel sealed with a solid ground glass stopper secured by copper wire. The glass vessel was placed in a metal bomb, solvent (ca. 20 ml) added to the bomb, and the bomb sealed with a screw-on top. The bomb was placed in an oven maintained at the desired temperature and rotated at a slight angle for the desired length of time. After thermolysis, the bomb was removed and cooled, and the glass vessel was carefully taken out. The solution was removed, the vessel rinsed with ethyl acetate (2 × 20 ml), and the solutions combined and evaporated in vacuo onto neutral alumina (ca. 10 g).

Thermolysis of Ferrocene-1,1′-disulfonyl Azide in Cyclohexane at 135°. A. For 4 Hr. The azide (0.84 g) in cyclohexane (30 ml, Na dried) was heated for 4 hr at 135°. After the thermolysis the solution was pale yellow and contained a moderate amount of black solid. The decomposition products were chromatographed on a column of neutral alumina (2.3 × 25 cm). Elution with benzene–ethyl acetate (98:2 v/v) gave starting azide (0.37 g, 43%). Elution with benzene–ethyl acetate (3:1 v/v) gave a yellow solid which, on recrystallization from light petroleum (bp 60–110°)–ethyl acetate, gave **1′-(*N*-cyclohexylsulfamyl)ferrocenesulfonyl azide (13,** 0.14 g, 26.2%): mp 115–116°; ir (KBr) 3235 (s), 2125 (s), 1370 (s), 1325 (s), 1195 (s), 1140 cm^{-1} (s); NMR ($CDCl_3$) δ 5.00–4.80 (m, 6 H), 4.71 (t, 2 H), 4.38 (d, 1 H, exchanges with D_2O), 3.15 (s, br, 1 H), and 2.0–0.9 (m, 1 OH); mass spectrum (70 eV) *m/e* (rel intensity) 453 (11), 452 ($M\cdot^+$, 45) 426 (100).

Anal. Calcd for $C_{16}H_{20}FeN_4O_4S_2$: C, 42.49; H, 4.46. Found: C, 42.55; H, 4.61.

Elution with ethyl acetate–ethanol (99:1 v/v) gave a yellow solid identified by its infrared spectrum as 1′-sulfamylferrocenesulfonyl azide (**12,** 4.7%).

No other compounds were eluted.

B. For 16 Hr. Elution with benzene–ethyl acetate (3:1 v/v) gave 1′-(cyclohexylsulfamyl)ferrocenesulfonyl azide (**13,** 0.066 g, 0.6%) (ir identical with that above).

Elution with benzene–ethyl acetate (1:1 v/v) gave *N,N′*-dicyclohexylferrocene-1,1′-disulfonamide (**8,** 0.094 g, 8.7%), mp 203–204°, identical with an authentic sample prepared above. Further elution with this solvent gave **1′-(*N*-cyclohexylsulfamyl)ferrocenesulfonamide (14,** 0.098 g, 10.7%) [from light petroleum (bp 60–110°)–ethyl acetate]: mp 136–137°; ir (KBr) 3340 (w), 3260 (m), 3220 (w), 1320 (s), 1150 (s), 1140 cm^{-1} (s); NMR ($CDCl_3$) δ 5.58 (s, 2 H, exchanges with D_2O), 4.92 (t, 2 H), 4.81 (t, 2 H), 4.65–4.60 (m, 4 H), 4.05 (s, 1 H, exchanges with D_2O), 3.10 (s, 1 H), and 2.0–0.8 (m, 1 OH); mass spectrum (70 eV) *m/e* (rel intensity) 428 (13), 427 (23), 426 ($M\cdot^+$, 100), 344 (40).

Anal. Calcd for $C_{16}H_{22}FeN_2O_4S_2$: C, 45.08; H, 5.20. Found: C, 45.37; H, 5.38.

Elution with ethyl acetate–ethanol (99:1 and 95:5 v/v) gave ferrocene-1,1′-disulfonamide (0.058 g, 7.8%) (ir spectrum identical with that of sample above). No other compounds were eluted.

Thermolysis of **6** in cyclohexane at 100° for 53 hr and work-up as above gave **9** (7.2%), **12** (2.7%), and **13** (9%), together with recovered **6** (34.4%).

Thermolysis of 6 in Benzene at 135°. A. For 4 Hr. The azide (0.68 g) was dissolved in benzene (30 ml, Na dried) and the solution heated for 4 hr at 135°. After thermolysis the solution was dark yellow and contained some black solid. The decomposition products were chromatographed on a column of neutral alumina (2.3 × 25 cm). Elution with benzene–ethyl acetate (98:2 v/v) gave starting azide (0.16 g, 23%). Elution with benzene–ethyl acetate (1:1 v/v) gave **1′-(*N*-phenylsulfamyl)ferrocenesulfonyl azide (15,** 0.081 g, 8.2%): mp 135–137° dec (from benzene–light petroleum); ir (KBr) 3240 (s), 2130 (s), 1365 (s), 1200 (s, broad), 1140 cm^{-1} (s); NMR ($CDCl_3$) δ 7.29–7.16 (m, 5 H), 6.70 (s, 1 H, exchanges with D_2O), 4.92 (t, 2 H), 4.86–4.75 (m, 4 H), and 4.67 (t, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 446 ($M\cdot^+$, 9), 420 (30), 104 (44), 77 (100).

Anal. Calcd for $C_{16}H_{14}FeN_4O_4S_2$: C, 43.06; H, 3.16. Found: C, 43.34; H, 3.34.

Elution with ethyl acetate–ethanol (99:1 v/v) gave 1′-sulfamylferrocenesulfonyl azide (**12,** 0.044 g, 8.2%) identical with the compound obtained above. Elution with ethyl acetate–ethanol (9:1 v/v) gave ferrocene-1,1′-disulfonamide (**9,** 0.002 g, trace) (ir).

No other compounds were eluted.

B. For 16 Hr. The azide (1.33 g) in benzene (30 ml, Na dried) was heated at 135° for 16 hr. The solution after thermolysis was very light yellow and contained a large amount of black solid in suspension. A small quantity (ca. 1 ml) of solution was removed and concentrated in a stream of nitrogen. Gas chromatographic analysis [OV-17 (20%) on Gas-Chrom Q, 6 ft × 3/16 in., He flow 80 ml/min; temperature program isothermal 400 sec at 70° then 6°/min] showed only one very small peak (retention time 1010 sec). Collection of this peak using capillary technique and mass spectroscopic analysis showed this to be aniline (*m/e* 93, fragmentation pattern identical with that of authentic sample of aniline), and its retention time was identical with that of aniline under these analysis conditions. No quantitative analysis was performed but the amount of aniline in the solution was very small. The remaining solution was chromatographed on a column of neutral alumina (2.3 × 25 cm). Elution with ethyl acetate–ethanol (9:1 v/v) gave ferrocene-1,1′-disulfonamide (0.062 g, 5.4%) (ir).

No other compounds were eluted.

C. In the Presence of Ferrocene for 3 Hr. The azide (0.88 g) was dissolved in benzene (40 ml, Na dried) and ferrocene (7.05 g) was added. The solution was heated at 135° for 3 hr and the products were chromatographed on a column of neutral alumina (2.3 × 45 cm). Elution with light petroleum–benzene (3:1 v/v) gave ferrocene (6.66 g, 94.5%). Elution with benzene–ethanol (99:1 v/v) gave starting azide (0.13 g, 14%). Elution with benzene–ethanol (98:2 v/v) gave 1′-(*N*-phenylsulfamyl)ferrocenesulfonyl azide (**15,** 0.13 g, 15.1%), identical with the sample previously characterized. Elution with benzene–ethanol (95:5 v/v) gave 1′-sulfamylferrocenesulfonyl azide (**12,** 0.11 g, 16.2%) (ir).

No other compounds were eluted.

The results of other reactions carried out at 135° in the presence of tetracyclone and tetracyanoethylene are given in Table II.

Thermolysis of Ferrocene-1,1′-disulfonyl Azide in Benzene at 100°. The azide (1.51 g) in benzene (35 ml, Na dried) was heated at 100° for 63 hr. After thermolysis the solution was dark yellow orange and contained a large amount of black solid. The decomposition products were chromatographed on a column of neutral alumina (2.3 × 25 cm). Elution with benzene and benzene–ethyl acetate (95:5 v/v) gave starting azide (0.81 g, 54%). Further elution with benzene–ethyl acetate (95:5 v/v) gave a yellow solid which, on recrystallization from light petroleum (bp 60–110°), gave light yellow crystals of ***N*-(1′-sulfonylazidoferrocenesulfonyl)-azepine (17,** 0.074 g, 9.4%): mp 109–110° dec; mass spectrum (70 eV) *m/e* (rel intensity) 446 ($M^{\cdot+}$, 2), 92 (100), 65 (24).

Anal. Calcd for $C_{16}H_{14}FeN_4O_4S_2$: C, 43.06; H, 3.16. Found: C, 43.12; H, 3.31.

Elution with benzene–ethyl acetate (85:15 v/v) gave a brown gum (0.007 g) which could not be identified. Elution with benzene–ethyl acetate (1:1 v/v) gave a yellow-brown gum (0.011 g) which could not be identified. Elution with ethyl acetate gave 1′-(*N*-phenylsulfamyl)ferrocenesulfonyl azide (**15,** 0.049 g, 6.3%) (ir). Elution with ethyl acetate–ethanol (98:2 v/v) gave 1′-sulfamylferrocenesulfonyl azide (0.054 g, 8.2%) (ir). Elution with ethyl acetate–ethanol (9:1 v/v) gave ferrocene-1,1′-disulfonamide (0.008 g, 1.4%) (ir).

No other compounds were eluted.

The reaction was repeated but heating was prolonged to 116 and 188 hr. The results are summarized in Table II, as are those of the reaction carried out in the presence of tetracyanoethylene.

Thermolysis of Ferrocene-1,1′-disulfonyl Azide in Mesitylene at 135°. A. For 3 Hr. The azide (0.74 g, 0.00188 mol) in mesitylene (30 ml, dried over molecular sieves) was heated at 135° for 3 hr. Chromatography on a column of neutral alumina (2.3 × 25 cm) and elution with benzene–ethyl acetate (95:5 v/v) gave starting azide (0.15 g, 20.4%). Elution with benzene–ethyl acetate (1:1 v/v) gave a light powder of **1′-(*N*-2,4,6-trimethylphenylsulfamyl)ferrocenesulfonyl azide (18,** 0.191 g, 26.2%): mp 136–139° dec [from light petroleum (bp 60–110°]; ir (KBr) 3250 (m, br), 2120 (s), 1365 (s), 1325 (m), 1195 (s), 1135 cm^{-1} (s); NMR ($CDCl_3$) δ 6.79 (s, 2 H), 5.97 (s, 1 H, exchanges with D_2O), 4.90 (t, 2 H), 4.77–4.67 (m, 6 H), 2.22 (s, 3 H), and 2.05 (s, 6 H); *m/e* (rel intensity) 488 ($M^{\cdot+}$, 5).

Anal. Calcd for $C_{19}H_{20}FeN_4O_4S_2$: C, 46.73; H, 4.13. Found: C, 46.87; H, 4.22.

Elution with benzene–ethanol (95:5 v/v) gave 1′-sulfamylferrocenesulfonyl azide (0.075 g, 13.5%) (ir).

No other compounds were eluted.

B. For 16 Hr. The decomposition products were chromatographed on a column of neutral alumina (2.3 × 25 cm) and eluted with benzene–ethyl acetate (1:1 v/v) to give ***N,N′*-di(2,4,6-trimethylphenyl)ferrocene-1,1′-disulfonamide (19,** 0.15 g, 11.6%): mp >280° (darkened rapidly above 200°) [from light petroleum (bp 60–160°)–ethyl acetate]; ir (KBr) 3310 (m, sh), 3295 (m), 3265 (m, sh), 1325 (s), 1135 cm^{-1} (s); NMR ($CDCl_3$) δ 6.84 (s, 4 H), 5.80 (s, 2 H, exchanges with D_2O), 4.66 (s, 8 H), 2.24 (s, 6 H), and 2.07 (s, 12 H); mass spectrum (70 eV) *m/e* (rel intensity) 582 (11), 581 (25), 580 ($M^{\cdot+}$, 65), 318 (32), 134 (100).

Anal. Calcd for $C_{28}H_{32}FeN_2O_4S_2$: C, 57.93; H, 5.56. Found: C, 57.90; H, 5.62.

Elution with ethyl acetate–ethanol (98:2 v/v) gave **1′-(*N*-2,4,6-trimethylphenylsulfamyl)ferrocenedisulfonamide (20,** 0.18 g, 17.2%): mp 195–196° dec [from light petroleum (bp 60–110°)–ethyl acetate]; ir (KBr) 3350 (m), 3270 (m), 1315 (s), 1195 (s), 1135 cm^{-1} (s); NMR (acetone-d_6) δ 7.9 (s, 1 H, exchanges with D_2O), 6.88 (s, 2 H), 6.46 (s, br, 2 H, exchanges with D_2O), 4.83 (t, 2 H), 4.67 (m, 6 H), 2.22 (s, 3 H), and 2.10 (s, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 464 (3), 463 (5), 462 ($M^{\cdot+}$, 19), 134 (43), 58 (27), 43 (100).

Anal. Calcd for $C_{19}H_{22}FeN_2O_4S_2$: C, 49.36; H, 4.80. Found: C, 49.56; H, 4.88.

Elution with ethyl acetate–ethanol (9:1 v/v) gave a ferrocene-1,1′-disulfonamide (0.101 g, 14.2%) (ir).

Thermolysis of 6 in Cyclohexene. The azide (0.85 g, 0.00215 mol) was added to cyclohexene (30 ml, freshly distilled, dried over molecular sieves) and the solution boiled under reflux under nitrogen (dry, O_2 free). After 11 hr a small quantity of orange needles was seen at the surface. On cooling, the yellow solution, which contained no dark solid, yielded a further small quantity of orange needles. A few crystals were removed from the solution, washed with light petroleum (2 × 10 ml), and dried in a stream of nitrogen for 2 min: ir (KBr) 1610 (s), 1310 (s), 1125 cm^{-1} (s). Gas chromatography of the solution [OV-17 (20%) on Gas-Chrom Q, 6 ft × 3/16 in., isothermal at 130°, He flow 80 ml/min] showed the presence of a small peak with retention time 171 sec, identified as cyclohexanone (vide infra). Addition of moist alimina to the reaction solution caused a marked (tenfold) increase in the area of the peak (relative to solvent peak area). Collection of this peak by capillary technique gave a colorless liquid, identical with an authentic sample of cyclohexanone (ir, MS, retention time). The decomposition products were chromatographed on a column of neutral alumina. Elution with ethyl acetate–ethanol (99:1 v/v) gave 1′-sulfamylferrocenesulfonyl azide (0.16 g, 20.2%) (ir). Elution with ethyl acetate–ethanol (9:1 v/v) gave ferrocene-1,1′-disulfonamide (0.211 g, 29.4%).

Thermolysis of 6 in Cyclohexene and Sodium Borohydride Reduction. The azide (1.49 g, 0.00377 mol) was dissolved in cyclohexene (35 ml, freshly distilled, dried over molecular sieves), molecular sieves (1 g) was added, and the solution was heated at 135° for 4 hr. The solution was orange and contained some orange needles mixed with a small amount of black solid. The thermolysis vessel was opened under a cone of nitrogen, a small magnetic stirring bar was introduced, and then sodium borohydride (0.45 g) in acetonitrile (20 ml, dried over molecular sieves) was added and a drying tube ($CaCl_2$) was placed on the vessel. The solution was stirred at room temperature for 3 hr in the absence of light and a second portion of sodium borohydride (0.25 g) was added. The solution was stirred overnight in the absence of light at room temperature and then aqueous acetic acid (5% v/v, 10 ml) was added dropwise. The aqueous layer was made basic to litmus with sodium carbonate, ethyl acetate (300 ml) was added, and the solution was dried ($CaCl_2$). The products were chromatographed on a column of neutral alumina (2.3 × 25 cm). Elution with benzene–ethyl acetate (1:1 v/v) gave *N,N′*-dicyclohexylferrocene-1,1′-disulfonamide (8, 0.82 g, 42.6%), identical with an authentic sample. Elution with ethyl acetate–ethanol (98:2 v/v) gave ferrocene-1,1′-disulfonamide (0.32 g, 24.3%) (ir).

Thermolysis of 6 in Freon 113. The azide (0.88 g, 0.00222 mol) was dissolved in Freon 113 and the solution was heated at 135° for 3 hr. The products were chromatographed on a column of neutral alumina (2.3 × 25 cm). Elution with benzene–ethanol (98:2 v/v) gave starting azide (0.11 g, 12.1%). Elution with benzene–ethanol (95:5 v/v) gave 1′-sulfamylferrocenesulfonyl azide (0.020 g, 2.8%) (ir). Elution with benzene–ethanol (9:1 v/v) gave ferrocene-1,1′-disulfonamide (0.023 g, 3.5%) (ir).

Ferrocenesulfonyl Hydrazide (23). To a stirred solution of ferrocenesulfonyl chloride (2.83 g, 0.01 mol) in benzene (12 ml) was added 50% hydrazine hydrate (1.60 g, 0.025 mol) dropwise over a 30-min period at 5–10°. The solution was kept at 50° for 6 hr, cooled, and evaporated in vacuo to give a yellow residue. This was recrystallized from absolute ethanol to give **ferrocenesulfonyl hydrazide (23,** 1.71 g, 61%): mp 135–140° dec; ir (KBr) 3400 (m), 3275–3270 (m, br), 1325 (s), 1130 cm^{-1} (s); NMR ($CDCl_3$) δ 5.65 (s, br 1 H, exchanges with D_2O, NH), 4.75 (t, $J_{2,3}$ = 1.7 Hz, 2 H, H_2 and H_5), 4.49 (t partially under 4.47, 1 H, H_3 and H_4), 4.47 (s, 5 H, H_1′–H_5′), and 3.48 (s, br, 2 H, exchanges with D_2O, NH_2); mass spectrum (70 eV) *m/e* (rel intensity) 281 (4), 280 ($M^{\cdot+}$, 31), 250 (60), 202 (33), 186 (90), 185 (44), 138 (100), 129 (67), 121 (68), 56 (79).

Anal. Calcd for $C_{10}H_{12}FeN_2O_2S$: C, 42.88; H, 4.32. Found: C, 43.14; H, 4.44.

Ferrocenyl Ferrocenethiolsulfonate (24). Ferrocenosulfonyl hydrazide (20 mg) was heated in an open test tube in an oil bath at 150–160° for about 25 min (until no further evolution of gas was noted). The gas evolved was basic. A small amount of yellow material solidified on the sides of the test tube above the level of the oil bath. This was shown to be ferrocene by comparison of its ir and MS with that of an authentic sample.

The yellow residue which remained at the bottom of the test

tube was recrystallized from benzene–light petroleum (bp 60–110°) to give golden yellow plates of **ferrocenyl ferrocenethiolsulfonate,** begins to darken at 180° and melts at 194–195° (dec): ir (KBr) 1320 (s), 1120 cm^{-1} (s); NMR ($CDCl_3$) δ 4.40 (m, 9 H), 4.32 (m, 2 H), 4.21 (s, 5 H), and 4.18 (m, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 467 (2), 466 ($M\cdot^+$, 7), 402 (52), 306 (22), 304 (24), 272 (24), 233 (21), 218 (36), 217 (100), 186 (29), 153 (39), 121 (40), 56 (31).

Anal. Calcd for $C_{20}H_{18}Fe_2O_2S_2$: C, 51.53; H, 3.89. Found: C, 51.66; H, 3.95.

2,4,6-Trimethylpyridinium Ferrocenesulfonylimino Ylide (22). Ferrocenesulfonyl hydrazide (7.00 g) and 2,4,6-trimethylpyrylium perchlorate[16] (5.68 g) in 95% ethanol (300 ml) were boiled under reflux for 24 hr under nitrogen. The solution was cooled and evaporated in vacuo to ca. 30 ml at 50°. A solution of potassium hydroxide (1.41 g) in water (9 ml) was added dropwise at 0° to the stirred solution. After 30 min at 0° the mixture was filtered cold and the filtrate evaporated onto basic alumina (10 g). The ylide was chromatographed on a column of basic alumina (2 × 45 cm) prepared in benzene. It was eluted with ethyl acetate–ethanol (95:5 v/v) and recrystallized from methanol–ether at −78° to give yellow-orange plates of **2,4,6-trimethylpyridinium ferrocenesulfonylimino ylide** (4.96 g, 52%): mp 180–182° dec; ir (KBr) 1290 (s), 1120 cm^{-1} (s); λ_{max} (EtOH) 212 nm (ε 37 000), 249 (13 360), 350 (730), and 426 nm (206); NMR ($CDCl_3$) δ 7.15 (s, 2 H, H_3 and H_5 of pyr), 4.44 (t, $J_{2,3}$ = 3.3 Hz, 2 H, H_2 and H_5), 4.35 (s, 5 H, H_1'–H_5'), 4.21 (t, $J_{2,3}$ = 3.3 Hz, 2 H, H_3 and H_4), 2.59 (s, 6 H, 2-CH_3 and 6-CH_3), and 2.39 (s, 3 H, 4-CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 385 (7), 384 ($M\cdot^+$, 33), 265 (36), 199 (12), 177 (29), 135 (21), 121 (100).

Anal. Calcd for $C_{18}H_{20}FeN_2O_2S$: C, 56.26; H, 5.24. Found: C, 56.58; H, 5.39.

Decomposition of the Ylide 22. A. Thermolysis. The ylide (0.34 g) in benzene (25 ml, Na dried) was heated at 175° for 10 hr. After cooling, the yellow solution and dark precipitate were removed, the liner was rinsed with benzene (3 × 10 ml), and the product mixture was evaporated onto neutral alumina (3 g). The mixture was chromatographed on a column of neutral alumina (1 × 20 cm). Elution with benzene–ethyl acetate (95:5 and 1:1 v/v) gave 2,4,6-trimethylpyridine (0.068 g, 71%), identical (ir, NMR, and MS) with an authentic sample. Further elution with benzene–ethyl acetate (1:1 v/v) gave ferrocenesulfonamide (0.11 g, 54%), identical (ir and NMR) with an authentic sample. Elution with ethyl acetate–ethanol (95:5 v/v) gave unchanged 2,4,6-trimethylpyridiniumferrocenesulfonylimino ylide (0.038 g, 11%).

B. Photolysis. The ylide (1.00 g) was dissolved in benzene (100 ml, Na dried) in a quartz photolysis vessel equipped with a nitrogen bubbler and drying tube ($MgSO_4$). The solution was purged with nitrogen (dry, O_2 free) for 30 min and then irradiated with 2537-Å lamps in a Rayonet reactor at a temperature of about 40°. Nitrogen was bubbled slowly through the solution during the irradiation. The progress of the photolysis was followed by removing an aliquot at regular intervals, evaporating to dryness under a cone of nitrogen, and observing the ir. After 72 hr no detectable change had occurred in the infrared spectrum. The solution was then removed, the vessel rinsed with benzene (2 × 20 ml), and the combined solutions chromatographed on a column of neutral alumina. Elution with ethyl acetate–ethanol (95:5 v/v) gave only starting ylide (0.72 g, 72%).

Experiments using 3000- and 3500-Å lamps gave similar results.

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Interaction of Alkali Metals with Unsaturated Heterocyclic Compounds. II. 2,4-Diphenylquinazoline

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2,4-Diphenylquinazoline (1) is reduced by sodium in tetrahydrofuran to a dianion **2.** Alkylation of this dianion with methyl iodide, *tert*-butyl bromide, 1,3-dihalopropanes, and 1,4-dibromobutane is described as well as acylation with ethyl chloroformate. Generally the alkylation products are 3,4-dihydroquinazoline derivatives but 1,4-dihydro derivatives are isolated in the case of methyl iodide and dimeric products formed by intermolecular alkylation are observed with 1,4-dibromobutane. The products formed by alkylation with *tert*-butyl bromide also contain compounds containing the alkyl group in the benzo ring. These products were also formed by the reaction of 1 with *tert*-butyllithium. In the case of acylation only 1,4-dihydroquinazoline derivatives were detected.

The reduction of conjugated bisimines by alkali metals in aprotic solvents has been examined in earlier studies.[1,2] In this report the combination of two imine groups conjugated through a carbon–nitrogen bond is studied by the reductive metalation of 2,4-diphenylquinazoline (1). This compound was selected since it both contained the desired conjugative arrangement and is similar to a compound examined in an earlier report,[2b] 2,3-diphenylquinoxaline.

Only the reduction of 1 in tetrahydrofuran (THF) by sodium was examined in detail, since under these conditions