the solution caused the rapid and complete transformation of **1a** into **1b**.

A portion of the solid residue was washed with cold carbon disulfide, which left undissolved the pure thieno[3,2-*b*]thiophen-2,5(3*H*,6*H*)-dione (**1a**), mp 104–105 °C; NMR (CS_2) δ 3.62.

Anal. Calcd for $C_6H_4O_2S_2$: C, 41.84; H, 2.35; S, 37.23. Found: C, 41.58; H, 2.34; S, 37.5. The remaining part of the solid residue and the part dissolved in CS_2 were chromatographed through a silica gel column using light petroleum ether (9:1) as eluent. The first fractions contained the yellow thieno[3,2-*b*]thiophen-2,5-dione[4] (**8**) (0.1 g), mp 155–156 °C. Fractions were then collected which contained the thieno[3,2-*b*]thiophen-2,5(6*H*, 7*H*)-dione (**1b**).

3,6-Dimethylthieno[3,2-*b*]thiophen-2,5(6*H*, 7*H*)-diones (2b and 2b′). The NMR spectrum of the crude residue (3.6 g) obtained from the reaction of **11** (7.5 g) showed the presence of compounds **2b** and **2b′** in the ratio of 60:40, together with lower amounts of **7a** ($R_3 = R_6 =$ Me) and **8** ($R_3 = R_6 =$ Me). The components were separated by column chromatography as described above for the reaction of **1**. The first fractions contained the yellow dione **8**[4] (0.2 g), mp 151–152 °C. Further elution afforded a mixture of the two isomers **2b** and **2b′** (2.5 g); crystallization from acetone–pentane gave pure **2b**, mp 130–132 °C. The solution of this compound, as well as those containing the two isomers in different proportions, when treated with HCl gas, gave a mixture of **2b** and **2b′** in the ratio of 85:15. Finally, fractions were collected containing compound **7b**[1] (0.5 g), mp 125–127 °C.

3,6-Diphenylthieno[3,2-*b*]thiophen-2,5-dione (8) ($R_3 = R_6 =$ Ph). The reaction carried out on **12** (2.7 g) afforded as the sole product the dione **8** (1.3 g), mp 224–225 °C.[4,13]

3-Methylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (5b). Reaction of **14** (5.5 g) afforded a solid residue (2.8 g) which was chromatographed to give the following fractions: (i) compound **8** ($R_3 =$ Me; $R_6 =$ H) (0.1 g), mp 91–93 °C,[4] (ii) compound **7a** ($R_3 =$ Me; $R_6 =$ H)[1] (0.7 g) which on standing gradually transforms in a mixture of **7a** and **7b**,[1] and (iii) compound **5b** (1.4 g), mp 109–110 °C from ethanol.

3-Phenylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (6b). The reaction carried out on 7.5 g of **15** afforded 3.7 g of residue which was worked up in the usual way to give (i) the dione **8** ($R_3 =$ Ph; $R_6 =$ H) (0.1 g), mp 124–126 °C,[1] (ii) compound **7a** ($R_3 =$ Ph; $R_6 =$ H)[1] (0.4 g), and (iii) the product **6b** (2.8 g), mp 145–147 °C from ethanol.

3-*tert*-Butylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (4b) and 6-*tert*-Butylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (4b′). The reaction was carried out on 5 g of **13**. The solid residue (3.2 g) was constituted by **8** ($R_3 = CMe_3$; $R_6 =$ H), **7a** ($R_3 = CMe_3$; $R_6 =$ H) and an equimolecular mixture of **4b** and **4b′**. The various components were separated by column chromatography in the usual way. The first fractions contained the dione **8**, mp 133–135 °C[4] (0.2 g); then 3-*tert*-butylthieno[3,2-*b*]thiophen-2(3*H*)-one, **7a** (0.7 g), mp 53–55 °C,[1] was collected. The following fractions contained mixtures, in different proportions, of **4b** and **4b′**; evaporation of the solvent left 2 g of residue. The mixture was crystallized from ethanol to afford pure 3-*tert*-butylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (**4b**), mp 108–110 °C (1.6 g). This compound, as well as the mixtures with the isomeric **4b′**, when treated with HCl gas, gave a mixture of **4b** and **4b′** in the ratio of 90:10.

Acknowledgment. Financial support from the CNR, Rome, is gratefully acknowledged.

Registry No.—**1a**, 65701-76-0; **1b**, 65701-77-1; **2b**, 61414-32-2; **2b′**, 65701-78-2; **4b**, 65701-79-3; **4b′**, 65701-80-6; **5b**, 65701-81-7; **6b**, 65701-82-8; **7a** ($R_3 = R_6 =$ Me), 56411-84-8; **7a** ($R_3 =$ Me; $R_6 =$ H), 56411-82-6; **7a** ($R_3 =$ Ph; $R_6 =$ H), 56411-81-5; **7a** ($R_3 = CMe_3$; $R_6 =$ H), 56411-80-4; **7b** ($R_3 = R_6 =$ Me), 56411-85-9; **7b** ($R_3 =$ Me; $R_6 =$ H), 56411-83-7; **8** ($R_3 = R_6 =$ H), 60749-71-5; **8** ($R_3 = R_6 =$ Me), 60749-72-6; **8** ($R_3 = R_6 =$ Ph), 51752-01-3; **8** ($R_3 =$ Me; $R_6 =$ H), 60749-73-7; **8** ($R_3 =$ Ph; $R_6 =$ H), 60749-76-0; **8** ($R_3 = CMe_3$; $R_6 =$ H), 60749-75-9; **9**, 65701-83-9; **10**, 25121-87-3; **11**, 56412-13-6; **12**, 65701-84-0; **13**, 65701-85-1; **14**, 65701-86-2; **15**, 65701-87-3; 3-mercaptothiophene, 7774-73-4; bromopinacolone, 5469-26-1; 3-thienylthiopinacolone, 65701-88-4; thieno[3,2-*b*]thiophene, 251-41-2; 3,6-dimethylthieno[3,2-*b*]thiophene, 56412-11-4; 3,6-diphenylthieno[3,2-*b*]thiophene, 21210-92-4; 3-methylthieno[3,2-*b*]thiophene, 1723-34-8; 3-phenylthieno[3,2-*b*]thiophene, 35022-15-2.

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Acid-Catalyzed Reaction of 1,6-Dioxaspiro[4.4]nonane with Ferrocene

William P. Norris

Organic Chemistry Branch, Chemistry Division, Code 3856, Michelson Laboratory, Naval Weapons Center, China Lake, California 93555

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1,6-Dioxaspiro[4.4]nonane reacts with ferrocene in the presence of aluminum chloride or boron trifluoride etherate to give 2-ferrocenyl-2-(3-hydroxypropyl)tetrahydrofuran (**5**). Treatment of **5** with methyl Grignard gives 4-methyl-4-ferrocenylheptane-1,7-diol (**7**). Reaction of **5** with trifluoroacetic acid gives ferrocenylbis(3-trifluoroacetoxypropyl)carbonium trifluoroacetate (**8a**). Treatment of **8a** with aqueous base gives 4-ferrocenyl-3-heptene-1,7-diol (**6**). With trifluoroacetic acid as catalyst, 1,6-dioxaspiro[4.4]nonane reacts with ferrocene to give a mixture of **5**, **6**, 4,4-diferrocenylheptane-1,7-diol (**3**), and 1,1′-bis[4-(4-ferrocenyl-1,7-dihydroxy)heptyl]ferrocene (**9**). Ferrocene and the ferrocene derivatives exist in an equilibrium condition in this reaction.

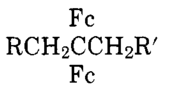
A few diferrocenylmethane derivatives with alkyl or substituted alkyl groups attached to the quaternary carbon have been reported.[1,2] They are made by the acid-catalyzed reaction of ketones with ferrocene. Compound **2**, R′ = CH_2CH_2OH, and derivatives of **2**, R′ = $CH_2CO_2CH_3$, have been used to chemically attach ferrocene derivatives onto specially designed polyurethane systems.[3] One objective of the present work was to prepare 4,4-diferrocenylheptane-1,7-diol (**3**) as a constit-

Table I. ^{1}H-NMR Spectra of 1,6-Dioxaspiro[4.4]nonane–Ferrocene Reaction Products

Compd	Registry no.	Chemical shift, δ (ppm) (Me$_4$Si)[a] CH$_2$CH$_2$	OCH$_2$	Fc	Other
5[b,d,e]	60583-71-3	1.2–2.5 (m)	3.56 (t, 6), 4.00 (t, 6)	3.9–4.3 (m, 9 H)	
8a[b,f]	65465-65-8	1.8–3.2 (m)	4.51 (t, 5)	4.98 (t, 2, 2 H), 5.01 (s, 5 H), 6.42 (t, 2, 2 H)	
6[b,d,e]	60635-84-9		3.65 (t, 6)	4.03 (s, 5 H), 4.25 (m, 4 H)	2.1–2.7 (m, =C(CH$_2$–)–) 5.68 (t, 7, =C(H)–) 1.4–2.0 (m, –CH$_2$–)
3[b,d,e]	60583-73-5	1.6–2.3 (m)	3.68 (t, 6)	4.06 (s, 10 H), 4.13 (m, 8 H)	
3[c,g]		1.4–2.1 (m)	3.44 (q, 5)	4.01 (s, 10 H), 4.11 (m, 8 H)	4.24 (t, 5, –OH)
9[c,g]	60583-70-2	1.3–2.2 (m)	3.42 (q, 5)	3.82 (m, 8 H), 4.03 (s, 10 H), 4.11 (m, 8 H)	4.22 (t, 5, –OH)
7[b,d,e]	60583-72-4	1.3–1.7 (m)	3.40 (t, 6)	3.9–4.3 (m, 9 H)	1.25 (s, –CH$_3$)

[a] Multiplicity of signal and coupling constant (Hz) in parentheses. [b] Measurements at 60 MHz, 27 °C. [c] Measurements at 100 MHz, 60 °C. [d] D_2O added. [e] $CDCl_3$. [f] CF_3CO_2H. [g] $(CD_3)_2SO$.

uent for directly incorporating ferrocenyl groups in polyurethane systems.[4]

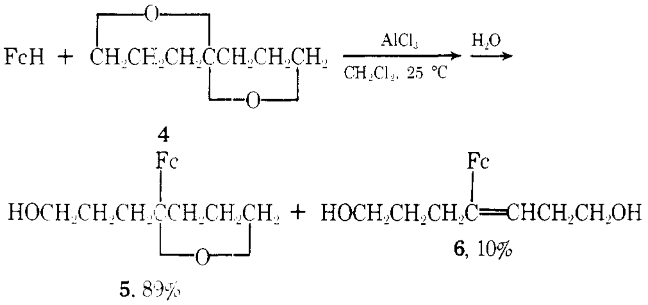


$$\overset{Fc}{\underset{Fc}{RCH_2CCH_2R'}}$$

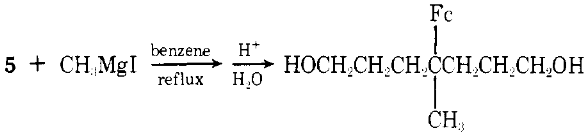
$$Fc = C_5H_5FeC_5H_4$$

1, R = R′ = H[1]
2, R = H; R′ = $CH_2CO_2CH_3$, CH_2CH_2OH[2]
3, R = R′ = CH_2CH_2OH

The acid-catalyzed reaction of the ketone derivative, 1,6-dioxaspiro[4.4]nonane[5] (**4**), with ferrocene could conceivably generate **3** with the desired four functional groups, two hydroxyl and two ferrocenyl, in one operation. It was found that the course of this reaction depends upon the catalyst used. With aluminum chloride the reaction goes half-way. The principal product isolated is 2-ferrocenyl-2-(3-hydroxypropyl)tetrahydrofuran (**5**). The small amount of 4-ferrocenyl-3-heptene-1,7-diol (**6**) is probably formed by reaction of **5** with aqueous hydrogen chloride formed when the reaction mixture is poured into water at the end of the reaction. Only one ketal ether ring is opened and only one ferrocenyl group is attached to the ketal skeleton even though 2 mol of aluminum chloride and 4 mol of ferrocene are used per mol of **4**. With boron trifluoride etherate as catalyst the principal product is also **5**. Treatment of **5** with methyl Grignard reagent[6] gives 4-methyl-4-ferrocenylheptane-1,7-diol (**7**), and with trifluoroacetic acid[7,8] ferrocenylbis(3-trifluoroacetoxypropyl)carbonium trifluoroacetate (**8a**)[9] is formed. The ferrocenylcarbonium ion, **8a**, is isolable (NMR[8,10,11] Table I) and stable in trifluoroacetic acid for 12 days at 25 °C in air. Treatment of **8a** with base abstracts a proton to give **6**. The small amount of **5** isolated may arise from some initial **5** that was oxidized by trifluoroacetic acid[12] to a ferricenium derivative, preventing ether cleavage, and subsequently recovered after reduction with ascorbic acid.



With trifluoroacetic acid as catalyst the reaction of **4** with ferrocene gives **3** and 1,1′-bis[4-(4-ferrocenyl-1,7-dihydroxy)heptyl]ferrocene (**9**) in addition to **5** and **6**.



$$5 + CH_3MgI \xrightarrow[\text{reflux}]{\text{benzene}} \xrightarrow[H_2O]{H^+} HOCH_2CH_2CH_2\overset{Fc}{\underset{CH_3}{C}}CH_2CH_2CH_2OH$$

7

$$5 \xrightarrow[25\ °C]{CF_3CO_2H} (CF_3CO_2CH_2CH_2CH_2)_2\overset{+}{C}Fc\ \ CF_3CO_2^-$$

8a

$$\xrightarrow[H_2O]{KOH} \mathbf{6},\ 84\% + \mathbf{5},\ 4\%$$

$$\underset{(2.15\ \text{mol})}{FcH} + \underset{(0.311\ \text{mol})}{4} \xrightarrow[CH_2Cl_2,\ 41\ °C]{CF_3CO_2H} \xrightarrow[H_2O]{\text{ascorbic acid}} \xrightarrow[CH_3OH]{KOH} \mathbf{5}\ (4.2\%) + \mathbf{6}\ (10\%)$$

$$+ \mathbf{3}\ (67\%) + \underset{\mathbf{9}\ (6.7\%)}{[(HOCH_2CH_2CH_2)_2C(Fc)]_2(C_5H_4)_2Fe}$$

The reaction proceeds as shown in the following scheme (eq 1–3). The product **3** (as **3a**) is

$$4 + FcH \xrightarrow{CF_3CO_2H} 5a \xrightarrow{CF_3CO_2H} 8a \qquad (1)$$

$$8a + FcH \overset{K_1}{\rightleftarrows} 3a \qquad (2)$$

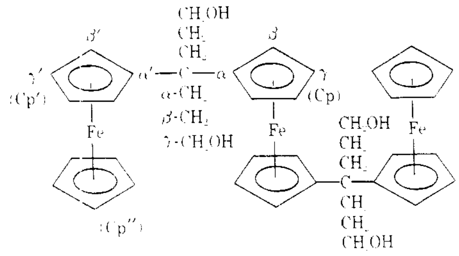
$$8a + 3a \overset{K_2}{\rightleftarrows} 9a \qquad (3)$$

formed from **8a** and ferrocene and similarly **9** (as **9a**) from **8a** and **3a**. Some of **5a** is trapped by oxidation to a ferricenium derivative and is recovered as **5** by reduction with ascorbic acid. Base converts **8a** into **6**. Reverse reactions of (2) and (3) were demonstrated qualitatively by treatment of **3a** and **9a** with trifluoroacetic acid (16 hr, 25 °C) followed by aqueous sodium hydroxide to give, in each case, mixtures of ferrocene, **6**, **3**, and **9**, resolvable by thin-layer chromatography on alumina and silica gel plates. An equilibrium ferrocene alkylation–dealkylation reaction involving an α-ferrocenylcarbonium ion has been reported.[13] Since reactions 2 and 3 are equilibrium reactions, it is evident that the concentration of **3a** with respect to **8a** and **9a** is favored by increased FcH concentration.[14] By using a 7 to 1 M ratio of FcH to **4**, as indicated in the previous experiment, **3** is the predominant product. By taking advantage of the equilibrium **9** could be prepared in quantity if desired.

Table II. ^{13}C-NMR Spectrum of 9, 25.14 MHz, 40 °C

^{13}C position[a]	No. of ^{13}C	Chemical shifts, ppm (Me_4Si)
Cp-α	2	99.66
Cp-β	4	66.86
Cp-γ	4	65.81
Cp′-α'	2	99.80
Cp′-β'	4	67.39
Cp′-γ'	4	66.52
Cp″	10	68.53
—C—	2	38.32
CH_2-α	4	27.87
CH_2-β	4	34.46
CH_2-γ	4	61.95

[a] Position designation:



9 (Cp = cyclopentadienyl)

Elemental analyses and proton NMR data are consistent with the structures of **3**, **5**, **6**, **7**, and **9**. In addition the ^{13}C NMR spectrum of the more complex molecule, **9**, is reported, Table II. A compound with a structure similar to **9**, 1,1′-bis[2-(2-ferrocenyl-4-carbomethoxybutyl]ferrocene, was isolated from the acid-catalyzed reaction of methyl levulinate with ferrocene.[2]

Experimental Section

Aluminum Chloride Catalyzed Reaction of 1,6-Dioxaspiro[4.4]nonane (4) with Ferrocene. To $AlCl_3$ (3.0 g, 0.023 mol), suspended in 100 mL of CH_2Cl_2 and flushed with N_2, was added dropwise over 15 min with stirring 1.28 g (0.0100 mol) of **4** and 7.44 g (0.0400 mol) of ferrocene dissolved in 100 mL CH_2Cl_2. The reaction temperature was initially 25 °C and warmed to 35 °C during the addition. Stirring was continued at 25 °C with N_2 atmosphere for 16 h. The reaction mixture was then poured into 200 mL of ice water and a little ascorbic acid was added to dispel the blue color (ferricenium ion) of the aqueous phase. The organic phase was separated and poured onto a 50 × 160 mm column of activity III (dry column grade) neutral alumina packed in CH_2Cl_2. Unreacted ferrocene, 5.52 g (0.0297 mol), was eluted with CH_2Cl_2. Using a 2:1 mixture of CH_2Cl_2 and $CH_3CO_2C_2H_5$ as solvent a large yellow band was eluted to give 2.80 g (0.008 92 mol) (89% yield) of 2-ferrocenyl-2-(3-hydroxypropyl)-tetrahydrofuran (**5**). Recrystallization from a 1:1 mixture of pentane and cyclohexane gave **5**, mp 50–53 °C.

Anal. Calcd for $C_{17}H_{22}O_2Fe$: C, 64.98; H, 7.06; Fe, 17.78; mol wt, 314. Found: C, 64.95; H, 6.81; Fe, 17.53; *m/e*, 314.

The remaining small yellow band at the top of the column was eluted with 4% CH_3OH in CH_2Cl_2 to give 0.31 g (0.000 99 mol) (10% yield) of 4-ferrocenyl-3-heptene-1,7-diol (**6**), mp 88–90 °C (after recrystallization from ethyl ether).

The reaction was repeated using ferrocene, 7.44 g (0.040 mol), **4**, 1.28 g (0.010 mol), and 3.6 mL (0.03 mol) of boron trifluoride etherate. After 2 h of stirring at 25 °C, workup gave 1.72 g (55% yield) of **5**.

Reaction of 5 with Methylmagnesium Iodide. Magnesium (1.2 g, 0.050 mol) was reacted with 7.1 g (0.050 mol) of methyl iodide in 25 mL of ether to form a solution of CH_3MgI. Then **5**, 1.08 g (0.0034 mol), was dissolved in 25 mL of ether and added to the CH_3MgI solution. A yellow precipitate formed immediately and then dissolved. Dry benzene (25 mL) was added and the ether was evaporated under reduced pressure. The benzene solution was refluxed for 2.5 h. Ice water was added to destroy excess Grignard reagent and then 6 N HCl was added to dissolve the magnesium salts. The benzene phase was separated and washed with saturated aqueous sodium chloride. The washed benzene phase was poured onto a dry 36 × 250 mm alumina column. The chromatogram was developed with ethyl acetate. The most rapidly moving band contained 0.46 g of **5**. The more slowly moving band was cut out of the column and extracted with methanol to give 0.38 g (0.0012 mol) (34% yield) of 4-methyl-4-ferrocenylheptane-1,7-diol (**7**), mp 109–110 °C. Recrystallization from carbon tetrachloride raised the mp to 111–112 °C.

Anal. Calcd for $C_{18}H_{26}O_2Fe$: C, 65.46; H, 7.94; Fe, 16.91; mol wt, 330. Found: C, 65.44; H, 8.26; Fe, 16.76; *m/e*, 330.

Preparation and Reaction of Ferrocenylbis(3-trifluoroacetoxypropyl)carbonium Trifluoroacetate (8a) with Base. Ferrocenylbis(3-trifluoroacetoxypropyl)carbonium trifluoroacetate was prepared by treating 2.80 g (0.00892 mol) of 2-ferrocenyl-2-(3-hydroxypropyl)tetrahydrofuran (**5**) dissolved in 15 mL of CH_2Cl_2 at 5 °C with 25 mL of CF_3CO_2H and then keeping it for 16 h at 25 °C. The volatiles were removed on the rotary evaporator (0.5 mm of pressure and 25 °C). The dark viscous residue was dissolved in 50 mL of CH_2Cl_2 and then treated with 100 mL of ice cold H_2O. The blue color of the aqueous phase was dispelled with ascorbic acid. Neutralization of the aqueous phase with 1 N KOH caused it to turn dark brown. The organic phase was separated and poured onto a 50 × 150 mm alumina (activity III, dry column grade) column. The chromatogram was developed and the first small band eluted with a 2:1 mixture of CH_2Cl_2 and $CH_3CO_2C_2H_5$ to give 0.12 g (4%) of **5**. The column was then treated with a 4% solution of CH_3OH in CH_2Cl_2 to elute the major yellow band leaving a small yellow band at the top of the column which was not investiated further. Evaporation of solvent left 2.35 g (84% yield) of 4-ferrocenyl-3-heptene-1,7-diol (**6**), mp 82–88 °C. This was recrystallized by dissolving it in 200 mL of ethyl ether, concentrating to 25 mL, and cooling to −10 °C overnight to give 1.56 g of glistening orange platelets of **6**, mp 88–90 °C.

Anal. Calcd for $C_{17}H_{22}O_2Fe$: C, 64.98; H, 7.06; Fe, 17.78; mol wt, 314. Found: C, 65.03; H, 7.00; Fe, 17.57; *m/e* 314.

The carbonium ion, **8a**, was formed by dissolving **5** (0.25 g) in 2 mL of CF_3CO_2H in an NMR tube. After 1 h at 25 °C, formation of **8a** was complete (see Table I for NMR).

Reaction of Ferrocenylbis(3-trifluoroacetoxypropyl)carbonium Trifluoroacetate (8a) with Ferrocene. **5** (1 g, 0.0032 mol) was dissolved in 10 mL of CF_3CO_2H at 25 °C and let stand for 2 h. The trifluoroacetic acid was removed under reduced pressure at 25 °C and ferrocene (5.41 g, 0.032 mol), dissolved in 25 mL of CH_2Cl_2, was added to the residue. The solution was stirred 40 h at 25 °C under an N_2 atmosphere and then treated with 50 mL of H_2O and enough ascorbic acid to reduce the ferricenium ion present. The phases were separated and the aqueous phase was extracted with 25 mL of CH_2Cl_2. The CH_2Cl_2 phases were combined, the CH_2Cl_2 was evaporated, and the residue was heated at 175 °C (0.25 mm) for 15 min to remove residual unreacted ferrocene. The nonvolatile residue was then dissolved in ethyl acetate containing 2% CH_3OH and chromatographed on a dry 36 × 250 mm alumina column. The major yellow band was excised, extracted with CH_3OH, and recrystallized from benzene to give 1.1 g (69% yield) of **3**, mp 168–171 °C. An additional recrystallization from CH_3OH gave **3**, mp 169–171 °C. No other bands of the column were separated and identified.

Reaction of Ferrocenylbis(3-trifluoroacetoxypropyl)carbonium Trifluoroacetate (8a) with 4,4-Diferrocenylheptane-1,7-diol (3). To 10 mL of CH_2Cl_2 was added 1.0 g (0.0020 mol) of **3**. To the stirred suspension (N_2 atmosphere, 25 °C) was added 0.84 g (0.0040 mol) of trifluoroacetic anhydride dissolved in 6 mL of CH_2Cl_2. The diol quickly dissolved. To this solution was added 0.63 g (0.0020 mol) of **5**, and 4 mL of CF_3CO_2H. After 40 h at 25 °C, N_2 atmosphere, the reaction mixture was added to ice water with enough ascorbic acid to discharge the blue color of the aqueous phase. The CH_2Cl_2 phase was separated and the volatiles were removed under reduced pressure to leave 2.5 g of residue. The residue was dissolved in 50 mL of CH_3OH and KOH was added until the solution remained basic. Most of the CH_3OH was removed under reduced pressure and then H_2O was added. The solids were dissolved in 4% CH_3OH in CH_2Cl_2 and chromatographed on alumina (dry clumn grade) to give 0.80 g of a mixture of **6** and **3**. TLC (SiO_2, ethyl acetate) showed approximately equal amounts of **3** and **6** in the mixture. Recrystallization of the mixture from CH_2ClCH_2Cl gave 0.40 g (0.00080 mol) of **3**, mp 169–171 °C. Continuing elution of the column with 10% CH_3OH in CH_2Cl_2 gave 0.40 g of material. Recrystallization from CH_3OH gave 0.30 g (0.00037 mol) of **9**, mp 202–204 °C.

Trifluoroacetic Acid Catalyzed Reaction of 4 with Ferrocene. To 1 L of CH_2Cl_2 was added 400 g (2.15 mol) of ferrocene and 40.0 g (0.311 mol) of **4**. The mixture was stirred and purged with N_2 for 5 min and then 296 g (2.60 mol) of trifluoroacetic acid was added. This reaction mixture was heated at reflux for 5.5 h while maintaining the N_2 atmosphere and then poured into 1.5 L of ice water containing 10 g of ascorbic acid. When the blue color of the aqueous phase disappeared, the organic phase was separated and the voltatiles were removed under reduced pressure (1 mm) with warming (80 °C) leaving 503 g of unreacted ferrocene and trifluoroacetylated ferrocene derivatives. This residue was hydrolyzed by stirring and heating to boiling in 1 L of CH_3OH containing 40 g (0.71 mol) of KOH. The resulting mixture was poured into 3 L of ice water and allowed to stand several hours to permit crystallization of products. The solids were separated by filtration and dried on the filter by sucking air through to leave 437 g (theoretical amount is 440 g) of products and unreacted ferrocene. This was extracted with five 3-L portions of boiling CH_2Cl_2 leaving 2.2 g of undissolved yellow powder (impure **9**).

The reaction mixture was separated by chromatography. The five 3-L portions of extract were poured onto an 85 × 440 mm alumina column, activity III (column packed in CH_2Cl_2), in the order in which they were taken. All unreacted ferrocene had been eluted by the time the last 3-L portion had been added. Evaporation of CH_2Cl_2 from this eluate left 298 g (1.60 mol) of ferrocene. There remained four well-defined bands on the column. The two bottom bands were eluted with CH_2Cl_2. The material from the first one, 0.7 g, was not identified. The next band, 4.0 g (0.013 mol, 4.1% yield), was identified by NMR as **5**.

The third (major) band was eluted with 4 L of 1% CH_3OH in CH_2Cl_2, 2 L of 2% CH_3OH in CH_2Cl_2, and then 6 L of 4% CH_3OH in CH_2Cl_2. (Starting elution with 4% CH_3OH in CH_2Cl_2 may cause 4,4-diferrocenylheptane-1,7-diol (**3**) to crystallize in the alumina column.) Evaporation of solvent left 114 g of a mixture of **6** and **3**. This mixture was dissolved in 1.8 L of boiling CH_2ClCH_2Cl, filtered, concentrated to 600 mL, and cooled to give 101.3 g (0.202 mol, 65% yield) of **3**, mp 168–171 °C. [Solubility of **3** is 0.38 g/100 mL of CH_2CCH_2Cl at 25 °C, indicating the presence of an additional 2.5 g of **3** in the mother liquor for a total of 103.8 g (0.207 mol, 67% yield) of **3**.] The presence of **6** and **3** in the mother liquor was shown by thin-layer chromatography on SiO_2 plates. A sample of **3** was recrystallized from CH_3OH, mp 169–171 °C.

Anal. Calcd for $C_{27}H_{32}Fe_2O_2$: C, 64.82; H, 6.45; Fe, 22.33; mol wt, 500. Found: C, 64.65; H, 6.50; Fe, 22.24; *m/e* 500.

After removal of the major band the alumina column was treated with 2 L of 6% CH_3OH in CH_2Cl_2 and 2 L of 10% CH_3OH in CH_2Cl_2. This developed the remaining band into two bands and eluted one to give 2.0 g of material which was not identified. The remaining band was removed with 25% CH_3OH in CH_2Cl_2. Evaporation of solvent left 10.4 g of material which was combined with the 2.2 g of undissolved yellow powder left after the initial extraction with CH_2Cl_2. This was dissolved in 4 L of hot CH_3OH, filtered, concentrated to 500 mL, and cooled to give 7.5 g (0.0092 mol, 5.9% yield) of **9**, mp 202–205 °C. [Solubility of **9** is 0.19 g/100 mL of CH_3OH at 25 °C, indicating the presence of an additional 0.95 g of **9** in the mother liquor for a total of 8.5 g (0.0104 mol, 6.7% yield) of **9**.] Another recrystallization from CH_3OH raised the melting point to 203–205 °C.

Anal. Calcd for $C_{44}H_{54}Fe_3O_4$: C, 64.89; H, 6.68; Fe, 20.57. Found: C, 64.87; H, 6.70; Fe, 20.11.

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Registry No.—**4**, 176-25-0; ferrocene, 102-54-5.

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Reaction of 6(7)-Diazopenicillanates and Diazocephalosporanates with Sulfenyl Chlorides. Preparation of 6(7)α-Methoxy-Substituted Thiol Penicillanates and Thiol Cephalosporanates

J. C. Sheehan* and Thomas J. Commons

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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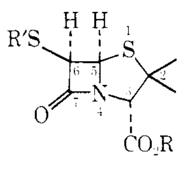
Reaction of diazo esters **3**, **10**, and **16** with sulfenyl chlorides in the presence of methanol gave 6(7)-α-methoxy thiol penicillanates and thiol cephalosporanates. Reaction of **10** and **16** with β,β,β-trichloroethoxycarbonylsulfenyl chloride in the presence of methanol gave the esters **12** and **19** which when treated with Zn–90% HOAc at 0 °C gave the mercaptans **13** and **20**. Mercaptans **13** and **20** were acylated by standard procedures.

A method has been developed in this laboratory for the preparation of sulfur analogues of penicillins and deacetoxycephalosporins of the general structures **1** and **2** where R′ can be either an alkyl group or an acyl group.[1] The isolation of cephalosporin derivatives from species of *Streptomyces* containing an α-methoxy group in the 7 position which exhibited greater activity than cephalosporin C against gram-negative organisms[2] suggested that the sulfur analogues **1** and **2** might also show increased activity with the introduction of an α-methoxy group in the 6(7) position. We wish to report here the preparation of such derivatives by reaction of the diazo esters **3**, **10**, and **16** with sulfenyl chlorides in the presence of methanol.



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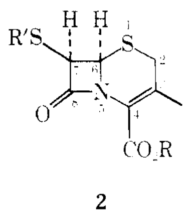

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