Thus, with **2a–c**, attack by **6** on the deactivated ring is slow relative to isomerization to **7**, resulting in the predominant formation of **4a–c** (Scheme II).

Experimental Section

Infrared spectra were taken on a Perkin-Elmer 580 or Infracord spectrophotometer. NMR spectra were recorded on a Perkin-Elmer R-24 or a Varian FT-80 and are expressed in parts per million downfield from Me_4Si. Melting points were determined in evacuated, sealed capillaries on a Thomas-Hoover apparatus and are corrected. Elemental analyses were obtained from the Analytical and Physical Section of Smith Kline & French Laboratories.

Preparation of the (Benzylamino)propyl Bromides 2. A solution of 0.10 mol of the appropriate aldehyde **1** and 0.10 mol of 3-amino-1-propanol in 250 mL of EtOH was stirred under N_2 at ambient temperature for 20 h. Solid $NaBH_4$ (0.13 mol) was added over 1 h, and the mixture was stirred for another 4 h. Acid–base extractive workup then afforded the crude (benzylamino)propyl alcohol, which was cooled in ice and dissolved in 100 mL of 48% HBr. The mixture was distilled until ca. 50 mL had been collected and was then cooled in ice. The resulting solid was filtered and recrystallized from EtOH or MeOH–Et_2O, affording the following compounds.

3-[(4-Chlorobenzyl)amino]-1-bromopropane Hydrobromide (2a): 37%; mp 212–214 °C (lit.[2] mp 205–206 °C). Anal. Calcd for $C_{10}H_{13}BrClN\cdot HBr$: C, 34.97; H, 4.11; N, 4.08. Found: C, 35.03; H, 4.16; N, 4.16.

3-[(2-Chlorobenzyl)amino]-1-bromopropane Hydrobromide (2b): 70%; mp 128–129.5 °C (lit.[3] mp 128–130 °C). Anal. Calcd for $C_{10}H_{13}BrClN\cdot HBr$: C, 34.97; H, 4.11; N, 4.08; Br, 46.52; Cl, 10.32. Found: C, 34.69; H, 4.18; N, 4.11; Br, 46.17; Cl, 10.03.

3-[(2,3-Dichlorobenzyl)amino]-1-bromopropane Hydrobromide (2c): 72%; mp 157–158 °C. Anal. Calcd for $C_{10}H_{12}BrCl_2N\cdot HBr$: C, 31.78; H, 3.47; N, 3.71. Found: C, 31.81; H, 3.42; N, 3.74.

Cyclization of the (Benzylamino)propyl Bromides (2). A mixture of 10.0 mmol of the appropriate compound and 0.56 g (10.5 mmol) of NH_4Cl was immersed in a preheated oil bath at the indicated temperature. The $AlCl_3$ (6.67 g, 50.0 mmol) was added over 5–10 min, causing the mixture to liquefy with the evolution of gas. After 15 min, the homogeneous mixture was dissolved in 50 mL of ice–3 N HCl, cooled in ice, and basified with 40% NaOH. The product was extracted with Et_2O, and the extract was washed with brine, dried over $MgSO_4$, and evaporated. TLC and VPC analyses of the reaction of **2c** indicated the presence of a single major product, which was isolated directly via the HCl salt. **2a** and **2b** each afforded two major products, which were purified by medium-pressure liquid chromatography (ca. 10% MeOH–CH_2Cl_2 on silica gel) prior to conversion to their HCl salts.

Cyclization of **2a** at 160 °C gave **6-chloro-4-methyl-1,2,3,4-tetrahydroisoquinoline (4a)**, 1.17 g (64%). For the hydrochloride: mp 194.5–195.5 °C (EtOH–Et_2O); IR (KBr) 818, 836, 846 cm^{-1}; NMR (D_2O) 1.37 (d, 3, J = 7 Hz, C-4 CH_3), 2.95–3.7 (m, 3, C-3 H and C-4 H), 4.34 (s, 2, C-1 H), 7.05–7.45 (m, 3, aromatic). Anal. Calcd for $C_{10}H_{12}ClN\cdot HCl$: C, 55.06; H, 6.01; N, 6.42; Cl, 32.51. Found: C, 55.14; H, 6.01; N, 6.42; Cl, 32.17. For the picrate, mp 183–185 °C (MeOH) (lit.[2] mp 174–175 °C).

Also obtained from **2a** was **7-chloro-2,3,4,5-tetrahydro-1*H*-2-benzazepine (3a)**, 0.26 g (14%). For the hydrochloride: mp 250–252 °C (EtOH–Et_2O); IR (KBr) 828 cm^{-1}; NMR (D_2O) 1.93 (m, 2, C-4 H), 2.97 (m, 2, C-5 H), 3.45 (m, 2, C-3 H), 4.34 (s, 2, C-1 H), 7.25 (m, 3, aromatic). Anal. Calcd for $C_{10}H_{12}ClN\cdot HCl$: C, 55.06; H, 6.01; N, 6.42; Cl, 32.51. Found: C, 54.81; H, 6.10; N, 6.24; Cl, 32.88. For the picrate, mp 193–196 °C (MeOH).

Cyclization of **2b** at 160 °C gave **8-chloro-4-methyl-1,2,3,4-tetrahydroisoquinoline (4b)**, 0.99 g (54%). For the hydrochloride: mp 178–179 °C (CH_3CN); IR (KBr) 785 cm^{-1}; NMR (D_2O) 1.36 (d, 3, J = 7 Hz, C-4 CH_3), 2.95–3.7 (m, 3, C-3 H and C-4 H), 4.38 (s, 2, C-1 H), 7.34 (s, 3, aromatic). Anal. Calcd for $C_{10}H_{12}ClN\cdot HCl$: C, 55.06; H, 6.01; N, 6.42; Cl, 32.51. Found: C, 55.40; H, 6.36; N, 6.56; Cl, 32.63. For the maleate, mp 140–141 °C (EtOH) (lit.[3] mp 130–133 °C).

Also obtained from **2b** was **5-chloro-4-methyl-1,2,3,4-tetrahydroisoquinoline (5)**, 0.25 g (14%). For the hydrochloride: mp 169–170 °C (CH_3CN); IR (KBr) 770, 782 cm^{-1}; NMR (D_2O) 1.38 (d, 3, J = 7 Hz, C-4 CH_3), 3.4–3.7 (m, 3, C-3 H and C-4 H), 4.38 (s, 2, C-1 H), 7.0–7.5 (ABC pattern, 3, J_{AB} = 7 Hz, J_{BC} = 7 Hz, J_{AC} = 2.5 Hz, aromatic). Anal. Calcd for $C_{10}H_{12}ClN\cdot HCl$: C, 55.06; H, 6.01; N, 6.42; Cl, 32.51. Found: C, 55.41; H, 6.06; N, 6.52; Cl, 32.60. For the maleate, mp 139–140 °C (EtOH–EtOAc).

Cyclization of **2c** at 170 °C gave **7,8-dichloro-4-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride (4c)**: 1.81 g (72%), mp 201–202 °C. Recrystallization from EtOH afforded an analytical sample: mp 210.5–212 °C (lit.[3] mp 199-203 °C); IR (KBr) 834 cm^{-1}; NMR (D_2O) 1.34 (d, 3, J = 7 Hz, C-4 CH_3), 2.9–3.65 (m, 3, C-3 H and C-4 H), 4.38 (s, 2, C-1 H), 7.25 and 7.40 (AB pattern, 2, J = 8 Hz, aromatic). Anal. Calcd for $C_{10}H_{11}Cl_2N\cdot HCl$: C, 47.56; H, 4.79; N, 5.55. Found: C, 47.56; H, 4.69; N, 5.82.

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Registry No. **1a**, 104-88-1; **1b**, 89-98-5; **1c**, 6334-18-5; **2a**, 40584-09-6; **2b**, 69739-56-6; **2c**, 69739-60-2; **3a**·HCl, 69739-52-2; **3a** picrate, 40584-17-6; **4a**·HCl, 73037-80-6; **4a** picrate, 73037-82-8; **4b**·HCl, 73037-83-9; **4b** maleate, 73037-85-1; **4c**·HCl, 73037-86-2; **5**·HCl, 73037-87-3; **5** maleate, 73037-89-5; 3-amino-1-propanol, 156-87-6; 3-[(4-chlorobenzyl)amino]-1-hydroxypropane, 73037-90-8; 3-[(2-chlorobenzyl)amino]-1-hydroxypropane, 69739-55-5; 3-[(2,3-dichlorobenzyl)amino]-1-hydroxypropane, 73037-91-9.

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Synthesis of (7-(Alkylthio)- and 7-(arylthio)cycloheptatriene)tricarbonyliron and -hexacarbonyldiiron Complexes

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Recently we have reported new methods for the functionalization of the cycloheptatriene skeleton starting from either tropone or tropenylium ions.[1] Perhaps the most striking result was that the treatment of tropone (**1**) with 1,2-ethanedithiol or 1,3-propanedithiol, under typical conditions for dithioketalization of ketones,[2] gave instead the dithiocycloheptatrienes **2**.[3]

This method could not be extended to simple thiols, such as methanethiol, which, in the case of **1** gave intractable mixtures.[4] Also, the use of zinc dichloride in diethyl ether as a catalyst proved not to be useful, because in the case of **1** and 1,2-ethanedithiol we obtained intractable mixtures.[5]

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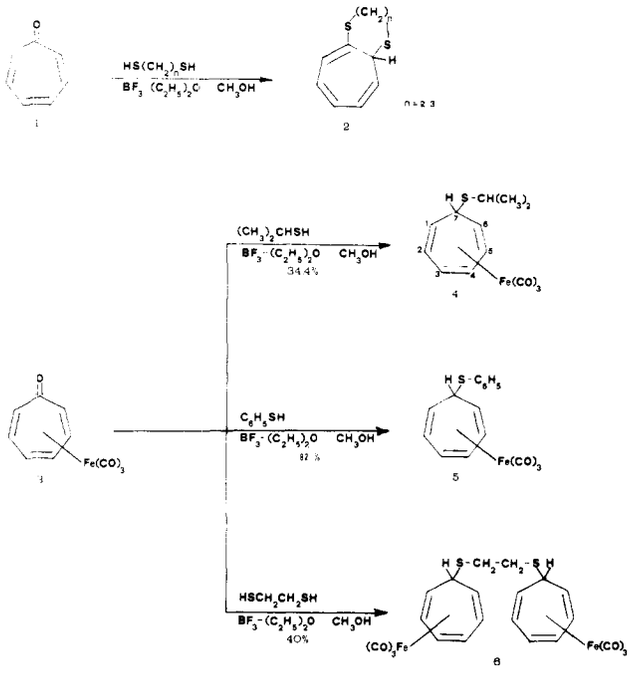


In no case were we able to obtain tropone dithioketals although they are conceivable intermediates both in the route from 1 to 2 and in the sigmatropic rearrangement of 1,7-dialkylcycloheptatrienes.[6] Therefore tropone dithioketals became interesting targets. Our present efforts toward the synthesis of such elusive species started from the observation that the ethylene dithioketal of 4,5-benzotropone could be easily obtained by the boron trifluoride method described above.[4] This was attributed to 4,5-bond fixation of tropone,[4] so that the idea was to immobilize two of the tropone π bonds[7] by coordination to iron tricarbonyl. We hoped to arrive at the iron tricarbonyl complexes of tropone dithioketals which could then be freed from the metal.

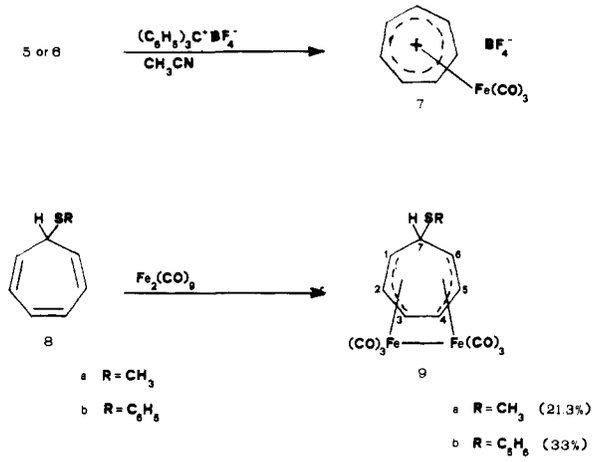
Although this expectation was not fulfilled, the results were interesting. In fact, on treatment of tropone–iron tricarbonyl (3) with either isopropyl mercaptan or thiophenol in the presence of boron trifluoride etherate in methanol, we obtained, respectively, the (7-(alkylthio)- or 7-(arylthio)cycloheptatriene)tricarbonylirons 4 and 5 in fair to high yields. The structures are based on the spectral data in the Experimental Section. The ^{1}H NMR spectra were particularly revealing. Thus, for 4 the methyls show up as a doublet at δ 1.05 further split into doublets by long-range coupling with H-7. The isopropyl methine gives a septet at δ 2.6 superimposed on a multiplet at δ 2.4 for H-2. The latter appeared as a pseudosinglet on double irradiation at δ 3.65 (H-1). H-7 gives a pseudotriplet at δ 1.9 due to coupling with H-1 and H-6. In fact, on irradiation at δ 3.65 (H-1) the triplet changed into a doublet. H-1 gives a ddd centered at δ 3.65 which originates from coupling with H-7 (J = 12 Hz), further split into doublets (J = 5 Hz, coupling with H-2) which, finally, are further split into doublets (J = 1 Hz) due to coupling with either H-6 or H-3. In fact, on double irradiation at the δ 1.9 triplet (H-7), the δ 3.65 signal changed into a much narrower multiplet. As to the remaining four ring protons, H-4 and H-5 give two low-field pseudotriplets, further split into small doublets, owing to the deshielding effect of $Fe(CO)_3$. The two pseudodoublets at δ 3.0 and 3.25 are then due to H-3 and H-6. In fact, on double irradiation at either δ 4.85 or 4.65 (H-4 and H-5) both the δ 3.0 and 3.25 signals became pseudosinglets showing only small couplings.

The case of 5 was similar. As can be judged from the ^{1}H NMR data, the spectrum of the cycloheptatriene moiety is very similar to that of 4. Double-resonance experiments led to very similar results to those above for 4.

Also with 1,2-ethanedithiol the dithioketalization product of 3 could not be obtained. In fact, both thiol ends of the dithiol behaved as simple thiols, as in the above cases of isopropyl mercaptan and thiophenol, to give 6. Structural proof for 6 is based on data similar to those discussed above for 4 and 5.

What remains unanswered about the structures 4, 5, and 6 is the relative spatial position of the iron and sulfide groups. However, comparison with (7-phenylcycloheptatriene)tricarbonyliron, where X-ray diffraction studies showed that phenyl and iron lie on opposite sides of the mean plane of the seven-membered ring,[8] suggests a similar relationship for iron and the alkylthio groups in 4–6.

Unfortunately, with (7-methoxycycloheptatriene)tricarbonyliron, which is the closest analogue to 4–6,[6] the spatial relationship between iron and the methoxy group has not been investigated. However, both (7-methoxycycloheptatriene)tricarbonyliron[9] and 5 and 6 show similar behavior toward electrophiles, giving the tropenyliumiron tricarbonyl salt 7.



The yields of 4–6 were not optimized because, whereas 5 was quite stable, both 6 and 4 were unstable. 4 was particularly labile, decomposing to a large extent during isolation to give tars. To some extent, intractable tars accompanied also 6 and 5, thus accounting for the material balance.

In particular, we proved that in the mixture leading to 5, diphenyl disulfide was present only in trace amounts, ruling out the thiol as the hydride source. In any case thiophenol could not have been expected as the only hydride source because, while thiophenol was used in stoichiometric amount, the yield of 5 is 82%. Possibly the solvent methanol is the source of hydride. This is conceivable if thiophenol is rapidly consumed by 3 to give, say, phenylthiotropenyliumiron tricarbonyl which then abstracts hydride from methanol. However, it proved difficult with our mixtures to establish whether methanol gives formaldehyde.

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The reductive addition of thiols to **3** to give **4–6** is interesting also because such compounds were not easily accessible by other routes. For example, **8a** and **8b** on treatment with $Fe_2(CO)_9$ failed to give any **4**- or **5**-type complexes. We obtained instead complexes of type $(C_7H_7SR)Fe_2(CO)_6$ to which we assign structures **9a** and **9b** mainly on the basis of the ^1H NMR data. In particular, in the case of **9b** on irradiation at the δ 1.95 broad triplet the multiplet at δ 5.2 became a doublet, which was then assigned to H-1 and H-6. The spectrum of **9a** was very similar.

However, also with both **9a** and **9b** the question of the spatial relationship between the iron moiety and alkylthio group remains unanswered.

The reagent of choice to bind a single $Fe(CO)_3$ unit to cycloheptatriene is $Fe(CO)_5$.[10] However, such a reaction only occurs at high temperatures[10] where our alkyl- and arylthiocycloheptatrienes undergo isomerization to a mixture of all possible alkyl- or arylthiocycloheptatrienes, thus depriving the method of any synthetic interest in our case.

Experimental Section

General Methods. Melting points (uncorrected) were determined with a Kofler hot-stage microscope. IR spectra were recorded on a Perkin-Elmer 283 spectrometer (ν in cm^{-1}), mass spectra on a Varian MAT CH7 spectrometer, and ^1H NMR spectra on Varian T-60 and JEOL SP-100 spectrometers. NMR data are given in δ with respect to Me_4Si as internal standard. UV spectra were recorded on a Unicam PS 800 spectrophotometer. Tetrahydrofuran, acetonitrile, methanol, and ethyl ether were purified, dried by standard procedures, and either stored over molecular sieves or used immediately after distillation. Fe_2CO_9[11] and (tropone)tricarbonyliron[12] were prepared according to literature procedures. Preparative layer chromatographic plates were homemade from neutral alumina (Merck Aluminum Oxid G).

[7-(Isopropylthio)cycloheptatriene]tricarbonyliron (4). To a solution of **3** (0.250 g, 1.01 mmol) in methanol (10 mL) were added with stirring under N_2 at room temperature 2-propanethiol (0.19 mL, 2.05 mmol) and boron trifluoride etherate (0.13 mL, 1.9 mmol). During 1 h of stirring the mixture turned from orange-red (due to **3**) to yellow. On evaporation of the solvent at reduced pressure an orange oil was left. Elution of this oil (benzene) on a neutral alumina layer gave **4**: 0.107 g (34%); R_f 0.36; orange-yellow semisolid; IR (Nujol) 2030, 1980 (CO), 1637 (C=C) cm^{-1}; ^1H NMR (C_6D_6) δ 4.85 (3 H, pseudo t of d, J = 5, 1 Hz, H-4 or H-5), 4.65 (3 H, pseudo t of d, J = 5, 1 Hz, H-4 or H-5), 3.65 (1 H, ddd, J = 12, 5, 1 Hz, H-1), 3.25 (1 H, dd, J = 7.2, 1 Hz, H-3 or H-6), 3.0 (1 H, dd, J = 7, 1 Hz, H-3 or H-6), 2.6 (1 H, septet, J = 6 Hz, $CH(CH_3)_2$) 2.4 (1 H, m, H-2), 1.9 (1 H, t, J = 12 Hz, H-7), 1.05 (6 H, dd, J = 6, 1 Hz, $CH(CH_3)_2$). Anal. Calcd for $C_{13}H_{14}FeO_3S$: C, 51.02; H, 4.57; S, 10.47. Found: C, 51.40; H, 4.60; S, 10.41.

[7-(Phenylthio)cycloheptatriene]tricarbonyliron (5). To a solution of **3** (0.136 g, 0.55 mmol) in methanol (5 mL) were added with stirring under N_2 at room temperature thiophenol (carefully freed from diphenyl disulfide, 0.060 mL, 0.58 mmol) and boron trifluoride etherate (0.07 mL, 0.57 mmol). During 75 min of stirring the mixture turned from orange-red to yellow. On evaporation of the solvent at reduced pressure an oily residue was left. The latter on addition of a little ethyl ether changed into yellow crystals of **5**: 0.154 g (82%); mp 121 °C (benzene); IR ($CHCl_3$) 2060, 1995 (CO), 1660 (C=C) cm^{-1}; ^1H NMR (C_6D_6) δ 7.3–6.9 (5 H, complex m, C_6H_5), 4.95–4.65 (2 H, complex m, H-4 and H-5; this multiplet is not resolved into two triplets, unlike the cases of **4** and **6**, because the spectrum was run at 60 MHz), 3.95 (1 H, ddd, J = 12, 5, 1 Hz, H-1), 3.15 (1 H, dd, J = 7.5, 1 Hz, H-3 or H-6), 2.95 (1 H, dd, J = 7.5, 1 Hz, H-3 or H-6), 2.5 (1 H, complex m, H-2), 1.9 (1 H, t, J = 12 Hz, H-7). Anal. Calcd for $C_{16}H_{12}FeO_3S$: C, 56.51; H, 3.53; S, 9.43. Found: C, 56.40; H, 3.45; S, 9.33. The reaction mixture was also checked for the presence of diphenyl disulfide by TLC on 0.2-mm-thick alumina (Macherey Nagel Düren N-UV 254, eluant petroleum ether–diphenyl disulfide, R_f 0.7; thiophenol, R_f 0.53). This was done both on the intact mixture after 75 min of stirring and on the residue after solvent evaporation at reduced pressure; only a trace of diphenyl disulfide was identified, possibly arising from air oxidation of thiophenol.

1,2-[Bis(7-thiocycloheptatrienyl)tricarbonyliron]ethane (6). To a solution of **3** (0.530 g, 2.15 mmol) in methanol (20 mL) were added with stirring under nitrogen at room temperature 1,2-ethanedithiol (0.20 mL, 2.4 mmol) and boron trifluoride etherate (0.27 mL, 2.15 mmol). During 1 h of stirring the orange-red color due to **3** faded while solid **6** precipitated and was filtered and ether washed to give 0.45 g (40%) of yellow crystals: mp 175 °C dec (from chloroform); IR (Nujol) 2070, 1980 (CO), 1640 (C=C) cm^{-1}; IR ($CHCl_3$) 2070, 2000 (CO), 1650 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.8 (1 H, t, J = 6 Hz, H-4 or H-5), 5.5 (1 H, t, J = 6 Hz, H-4 or H-5), 3.7 (1 H, ddd, J = 12, 5, 1 Hz, H-1) 3.4 (1 H, d, J = 7.5 Hz, H-3 or H-6), 3.2 (1 H, d, J = 6 Hz, H-3 or H-6), 2.75 (4 H, s, CH_2CH_2), 2.3 (1 H, complex m, H-2), 2.0 (1 H, t, J = 12 Hz, H-7); mass spectrum, m/e 554 (1.4%, $M^+ - Fe(CO)_3$, CO, CH_3), 315 (1.0%, $M^+ - Fe(CO)_3$, 3 CO, CH_3), 261 (1%, $M^+ - 2Fe(CO)_3$, CH_3), 176 (9.1%), 108 (11.2%), 91 (3.5%), 79 (100.0%), 77 (35.0%); UV (CH_3OH) λ_{max} 262 nm. Anal. Calcd for $C_{22}H_{18}Fe_2O_6S_2$: C, 47.69; H, 3.25; S, 11.57. Found: C, 47.36; H, 3.20; S, 12.00.

Tropenyliumtricarbonyliron Tetrafluoroborate (7).[9] To 0.191 g (0.578 mmol) of trityl tetrafluoroborate dissolved in a minimum amount of dried acetonitrile was added 0.58 mmol of either **5** or **6**. After 15 min dried ethyl ether was added; pale yellow crystals precipitated which were filtered under N_2, rinsed with dried ether, and then dried in vacuo to yield 0.120 g (90.3%) of **7**: mp 112 °C dec; IR (Nujol) 2110, 2070 (CO) cm^{-1}.

7-(Phenylthio)cycloheptatriene (8b). To 0.765 g (4.30 mmol) of tropenylium tetrafluoroborate in 8.1 mL of 0.1 M HCl was added a stoichiometric amount of thiophenol. After 19 h the mixture was extracted with ethyl ether and the ether layer was washed with 10% aqueous sodium chloride and then dried over sodium sulfate. **8b** was purified by TLC (silica gel, Merck Kieselgel 60 PF 254) with petroleum ether–ethyl ether (90:10) as eluant to give **8b**, 0.558 g (68%), as a pale yellow oil: R_f 0.6; ^1H NMR ($CDCl_3$) δ 7.2 (5 H, m, C_6H_5), 6.5 (2 H, t, J = 3 Hz, H-3 and H-4), 6.4–6.0 (2 H, complex m, H-2 and H-5), 5.5 (2 H, dd, J = 8, 6 Hz, H-1 and H-6), 3.9 (1 H, t, J = 6 Hz, H-7).

[7-(Methylthio)cycloheptatriene]hexacarbonyldiiron (9a). To a solution of **8a**[13] (0.558 g, 4.04 mmol) in ethyl ether (12 mL) was added $Fe_2(CO)_9$ (0.735 g, 2.02 mmol). The mixture was refluxed for 5 h and filtered when still warm, and the filtrate was evaporated at reduced pressure. The red oily residue was chromatographed on a neutral alumina layer with benzene as eluant. The red (R_f 0.9) band gave **9a**, 0.36 g (21%), as a red oil; IR (Nujol) 2070, 2020, 2000, 1990, 1970, 1910 cm^{-1}; UV (CH_3OH) λ_{max} 332 nm; ^1H NMR ($CDCl_3$) δ 6.6 (2 H, t, J = 3 Hz, H-3 and H-4), 6.2 (2 H, dd, J = 9, 3 Hz, H-2 and H-5), 5.3 (2 H, dd, J = 9, 3 Hz, H-1 and H-6), 2.1 (3 H, s, CH_3), 2.0 (1 H, br t, J = 3 Hz, H-7). Anal. Calcd for $C_{14}H_{10}Fe_2O_6S$: C, 40.23; H, 2.39; S, 7.67. Found: C, 40.10; H, 2.34; S, 7.52.

[7-(Phenylthio)cycloheptatriene]hexacarbonyldiiron (9b). To a solution of 7-(phenylthio)cycloheptatriene (**8b**) (0.588 g, 2.94 mmol) in ethyl ether (10 mL) was added $Fe_2(CO)_9$ (1.388 g, 3.8 mmol). Refluxing and workup as described above for **9a** gave **9b**, 0.461 g (33%), as a red oil which crystallized from petroleum ether at −20 °C to give red violet needles: mp 129 °C; IR (isooctane) 2070, 2030, 2000, 1985, 1965, 1905 (all bands attributable to CO, see text) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (5 H, br s, C_6H_5), 6.6 (2 H, m, H-3 and H-4), 6.2 (2 H, dd, J = 9, 3 Hz, H-2 and H-5), 5.2 (2 H, dd, J = 9, 3 Hz, H-1 and H-6), 1.95 (1 H, br t, J = 3 Hz); UV (CH_3OH) λ_{max} 340 nm. Anal. Calcd for $C_{13}H_{12}Fe_2O_6S$: C, 47.54; H, 2.50; S, 6.68. Found: C, 47.30; H, 2.40; S, 6.50.

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Haloaziridines. 3. Methanolysis of Some *gem*-Dichloroaziridines[1]

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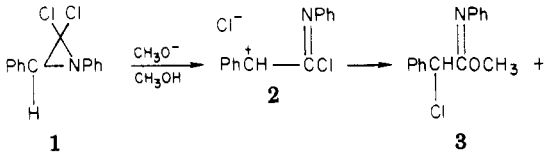
The methanolysis of 1,3-diphenyl-2,2-dichloroaziridine (1) has been reported to afford in high yield a mixture of the α-chloroimino ester 3 (38%) and the α-methoxyimino ester 4 (62%) in methanol–methoxide solution.[3] These



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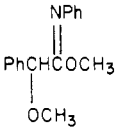

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products are consistent with those observed from hydrolysis,[4] aminolysis,[5] and pyrolysis[6] of *gem*-dichloroaziridines, and carbonium ion 2 has been proposed as an intermediate in the formation of these products. In contrast to these results, the reaction of 1 in methanol in the absence of methoxide is reported to afford a mixture of esters 5 and 6 in the same approximate ratio as the ratio of 3 to 4 and anilinium chloride.[3] Ichimura and Ohta have reported that the ethanolysis of 1 affords ethyl 2-chloro-2-phenylacetate and anilinium chloride.[7]

$$1 \xrightarrow{CH_3OH} \underset{5}{PhCHClC(O)OCH_3} + \underset{6}{PhCH(OCH_3)C(O)OCH_3} + PhNH_3^+Cl^-$$

The possible hydrolysis of the imino esters to 5 and 6 was tentatively eliminated by demonstrating their formation from 1 in high yield with anhydrous methanol. Since water was eliminated as the source of the carbonyl oxygen, the other logical source would be methanol, and an ortho ester intermediate has been proposed.[7] Our initial attempts to observe an ortho ester intermediate by NMR spectroscopy of the reaction mixture were unsuccessful due to the five signals in the δ 3–5.5 region attributed to the products. The NMR spectrum of the reaction mixture was simplified by pyrolysis of 1 to the imidoyl chloride 7.

$$1 \rightarrow \underset{7}{PhCHClC(NPh)Cl} \xrightarrow{CH_3OH} 5 + PhNH_3^+Cl^-$$

Quenching the imidoyl chloride 7 with anhydrous methanol afforded 5 and anilinium hydrochloride in high yield; however, absorptions attributable to an ortho ester intermediate were not observed.

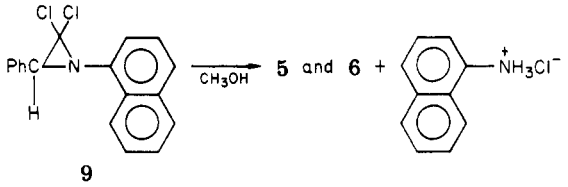
There is precedent for the formation of ortho esters from imidoyl chlorides[8] and for the acid-catalyzed decomposition of ortho esters to esters.[9] The decomposition of ortho ester intermediate 8 should form methyl ether and/or methyl

$$7 \xrightarrow{CH_3OH} \underset{8}{PhCHClC(OCH_3)_3} + HCl \rightarrow 5 + CH_3OCH_3 \text{ and/or } CH_3Cl$$

chloride. To determine if these gaseous products were formed, we examined the methanolysis of 1 on a multipurpose vacuum line, and a 50% yield of a mixture of methyl chloride and methyl ether was obtained in a 3:1 ratio, respectively.

The imino ester 3 was also prepared and converted to 5 under anhydrous reaction conditions and in the presence of small amounts of water. Consequently, the methanolysis of 1 appears to follow the typical ring-opening reaction to the expected imino esters. Reaction of the imino esters with methanol and the generated hydrogen chloride gives rise to 5 and 6.

The only reported alcoholysis reaction of a *gem*-dichloroaziridine in this series is 1. To determine the scope of this reaction, we examined the methanolysis of several additional *gem*-dichloroaziridines. The methanolysis of 1-(1-naphthyl)-3-phenyl-2,2-dichloroaziridine (9) gave the



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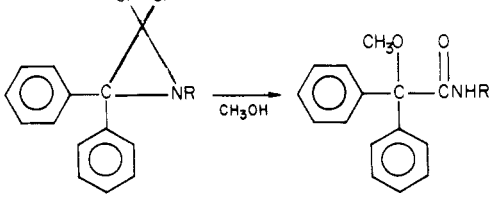
expected mixture of 5 and 6 and naphthylamine hydrochloride in high yield. The methanolysis of 1,3,3-triphenyl-2,2-dichloroaziridine (10a) and 1-benzyl-3,3-diphenyl-2,2-dichloroaziridine (10b) afforded the amide 11 as the major product. The methanolysis of 10b afforded



10a, R = Ph
b, R = $PhCH_2$

11a, R = Ph
b, R = $PhCH_2$

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