the bromination of 3-phenylthiophene may indicate that the steric requirements of the brominating species are important. Bromination with molecular bromine is known to have a large selectivity factor[4] although biphenyl itself does not follow the selectivity rule, the reason for this being a matter of controversy.[6-8] Some authors consider the large para:ortho ratio (97.5:2.5)[9,10] in the bromination of biphenyl with molecular bromine to be mainly due to the greater importance of conjugative electron release with a neutral reagent in combination with increased stability of "para-quinoid" over "ortho-quinoid" transition states and not so much to the steric requirements of the brominating agent.[6,11] However, it is possible that the seeming discrepancies may be due to a difference in the mechanism of bromination of benzenes and thiophenes, an addition–elimination being involved in the latter case.

In contrast to the results cited above bromination using NBS in carbon tetrachloride with benzoyl peroxide initiator led exclusively to the 2 isomer. No 5 isomer could be detected gas chromatographically. Recent work has shown that benzylic bromination with NBS proceeds by a free-radical chain mechanism with a bromine radical as the hydrogen-abstracting agent,[12-14] the bromine radical being produced from molecular bromine formed from the reaction between NBS and hydrogen bromide. Much less appears to be known about the mechanism of nuclear bromination of activated aromatics by NBS. The quite different isomer distribution with 3-phenylthiophene makes it rather unlikely that molecular bromine could be the brominating agent in the NBS case unless the change in solvent (carbon tetrachloride in place of boiling acetic acid) has a great effect. A direct radicaloid substitution reaction as suggested for the bromination of naphthalene[15] under certain conditions is a possibility. More likely, perhaps, is the free-radical addition of bromine across the 2,3 positions followed by loss of hydrogen bromide. The report of Ross[16] that a rapid ionic path exists in polar media is interesting but doesn't seem applicable in this case.

Although further studies are necessary in order to elucidate the mechanistic details, the differences are very fortunate from the preparative point of view making both 2-bromo-3-phenylthiophene and 5-bromo-3-phenylthiophene available as possible useful synthetic intermediates.

Experimental Section

Nmr spectra were taken on a Varian A-60 instrument; gas chromatography was done on a F & M 810 with hydrogen flame detectors and an Aerograph Autoprep Model A-700.

Bromination of 3-Phenylthiophene with N-Bromosuccinimide.—A mixture of 1.6 g (10 mmoles) of 3-phenylthiophene, 1.8 g

(10 mmoles) of N-bromosuccinimide (recrystallized from glacial acetic acid), a few milligrams of benzoyl peroxide, and 60 ml of carbon tetrachloride were refluxed for 49 hr after which time examination by glpc (diethylene glycol succinate, 6 ft, 190°) showed that the starting material had disappeared and a single product peak had appeared. The solution was filtered, washed three times with 5% potassium hydroxide solution and once with water, and dried over magnesium sulfate. The solvent was removed and the red residue was chromatographed on 2 × 20 cm of Grade 1 Merck alumina using 100 ml of reagent grade benzene as eluent. Removal of the benzene left 2.28 g. (95%) of a transparent liquid, bp 104–110° (0.25 mm). The nmr spectrum in acetone, in addition to the phenyl protons, showed two doublets centered at τ 2.56 and 2.94 (J_{45} = 5.4 cps) positively identifying the product as 2-bromo-3-phenylthiophene.[3] The material did not appear to be stable for long periods and repeated attempts at analysis gave erratic results. The bromide was thus converted to the solid carboxylic acid for analysis.

3-Phenyl-2-thiophenecarboxylic Acid.—Treatment of 0.68 g (2.84 mmoles) of freshly prepared 2-bromo-3-phenylthiophene with 0.20 g (8.2 mg-atoms) of magnesium in ether gave the Grignard reagent. Addition of solid carbon dioxide and work-up of the reaction mixture gave 0.56 g (88%) of 3-phenyl-2-thiophenecarboxylic acid, mp 201–204° (lit.[17] mp 205–206°). Its nmr spectrum (acetone) showed, in addition to the phenyl absorptions, two doublets at τ 2.35 and 2.90 (J_{45} = 5.2 cps).

Anal. Calcd for $C_{11}H_8O_2S$ (204.2): C, 64.68; H, 3.95; S, 15.70. Found: C, 64.92; H, 3.88; S, 15.38.

The same compound has also been obtained from the hypobromite oxidation of 2-acetyl-3-phenylthiophene.[5]

Bromination of 3-Phenylthiophene with Molecular Bromine.—Bromine (10.0 g, 0.063 g-atom) in 100 ml of glacial acetic acid was added dropwise to 10.0 g (0.063 mole) of 3-phenylthiophene in 130 ml of glacial acetic acid and the mixture was refluxed for 5 hr, cooled, and poured into water to yield 11.5 of crude product. Examination by glpc (30% Apiezon L 270°) showed four peaks. The first one had the same retention time as the starting material, the second (9.2 min) and third (12.7 min) had relative areas of 1:2, and finally a weak peak (18.1 min) probably owing to a dibromo derivative was observed. Through preparative gas chromatography the components with retention times of 9.2 and 12.7 min were obtained pure. The first component had the same infrared and nmr spectrum as 2-bromo-3-phenylthiophene, while the second component was 5-bromo-3-phenylthiophene, mp 75–77°, after recrystallization from aqueous ethanol. The nmr spectrum (dimethyl sulfoxide), in addition to the phenyl protons, showed two doublets centered at τ 2.13 and 2.29 (J_{24} = 1.8 cps). Pure 5-bromo-3-phenylthiophene could also be obtained by recrystallization from aqueous ethanol of the crude reaction product.

Anal. Calcd for $C_{10}H_7BrS$ (239.1): C, 50.23; H, 2.95; S, 13.41. Found: C, 50.54; H, 3.35; S, 13.36.

(17) H. Fiesselmann and H. Habicht, German Patent 1,092,929 (1962); *Chem. Abstr.*, **57**, 5895a (1962).

Reactions of Certain Ferrocene Compounds Leading to a Ferrocenyl Ethyl Ether[1a]

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Recently, in connection with the proof of structure of the benzophenone adduct of lithiodimethylaminomethylferrocene, its methiodide (I) was converted

(6) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 1242 (1962).
(7) R. Baker, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 2136 (1963).
(8) R. C. Neuman, Jr., *J. Am. Chem. Soc.*, **84**, 3025 (1962).
(9) E. Berliner, G. L. Zimmerman, and G. C. Pearson, *J. Org. Chem.*, **26**, 1633 (1961).
(10) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **84**, 1238 (1962).
(11) P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 40 (1956).
(12) C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3134 (1963).
(13) C. A. Russel and K. M. Desmond, *ibid.*, **85**, 3129 (1963).
(14) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963).
(15) F. R. Mayo and W. B. Hardy, *ibid.*, **74**, 911 (1952).
(16) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **80**, 4327 (1958).
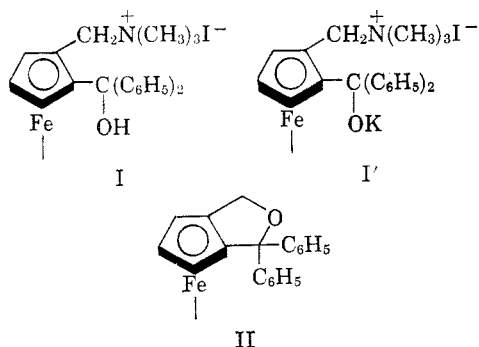
through potassio salt I′ to cyclic ether II by extended refluxing in 1,2-dimethoxyethane (monoglyme).[2]

In the present investigation, carbinol quaternary ion I was found to react with sodium ethoxide in ethanol, silver oxide in aqueous ethanol, and 2% aqueous ethanolic acetic acid to form carbinol ethyl ether III; none of the isomeric carbinol ether IV was isolated.
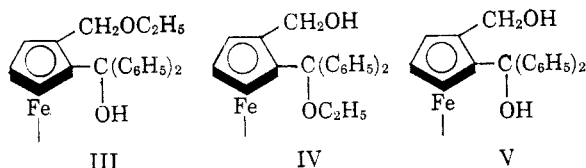
Also treatment of cyclic ether II and diol V with the acidic reagent afforded III. These reactions are summarized below.
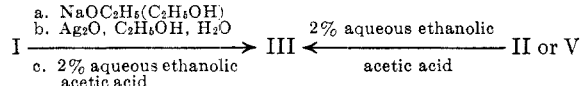
Support for the structure assignment of III was gained from elemental analysis and from absorption spectra. Thus, its infrared spectrum exhibited, in addition to 9- and 10-μ bands characteristic of an unsubstituted cyclopentadienyl ring in a ferrocene,[3] bands at 7.39 and 8.93 μ indicative of a tertiary alcohol,[4] and a strong absorption at 9.15 μ suggestive of a CH_2OCH_2 linkage;[5] also a band at 2.88 μ for hydroxyl was present. Utilization of a recent nmr technique[6] allowed determination of the OH group multiplicity in III and thereby the substitution on the alcohol function. The nmr spectrum in specially dried dimethyl sulfoxide showed an OH singlet at τ 4.1 which is close to the tertiary alcohol singlet at 4.35 for diphenylhydroxymethylferrocene and different from the primary alcohol triplet at 5.35 for hydroxymethylferrocene under the same conditions. In addition the nmr spectrum of III in $CDCl_3$ exhibited a five-proton singlet corresponding to an unsubstituted cyclopentadienyl ring at τ 5.70 and a methyl triplet centered at 8.86. Unfortunately, resolution of the remaining ring and methylene protons could not be effected.

(2) D. W. Slocum, B. W. Rockett, and C. R. Hauser, *J. Am. Chem. Soc.*, **87**, 1241 (1965).

(3) M. Rosenblum, Ph.D. Thesis, Harvard University, 1953; M. Rosenblum, *Chem. Ind.* (London), 953 (1958).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 96. Apparently there is no agreement on the position of these tertiary alcohol bands; this assignment is consequently of limited value. *Cf.* C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, p 188.

(5) *Cf.* ref 4, p 115.

(6) O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1258 (1964).

It might appear that the reaction of carbinol quarternary ion I with sodium ethoxide to form III involved the intermediate formation of cyclic ether II; this was shown not to be the course of the reaction, however, since II was found not to afford III under similar conditions. Evidently I reacted with sodium ethoxide by a Williamson-type displacement to form directly carbinol ethyl ether III. This furnished further evidence that the carbinol ethyl ether obtained was III, not IV, since the latter could presumably have arisen only through the intermediate formation of cyclic ether II. The reaction of carbinol quaternary ion I with the acidic reagent was apparently an ethanolysis. This reaction as well as that of the diol V with the acidic reagent might have involved the intermediate formation of cyclic ether II, since the latter was converted to III under similar conditions.

Experimental Section[7]

Synthesis of Ethyl 2-Diphenylhydroxymethylferrocenylmethyl Ether (III). A. Sodium Ethoxide Method.—The methiodide (I) of 2-(α,α-diphenylhydroxymethyl)dimethylaminomethylferrocene[2] (1.7 g, 3 mmoles) was refluxed for 48 hr in 20 ml of absolute ethanol containing 15 mmoles of sodium ethoxide. It was noted that a gas basic to indicator paper was given off over the first 24 hr. Some of the product crystallized from solution upon standing. This was isolated on a Büchner funnel and set aside. The remainder was recovered by stripping off some of the alcohol, adding water to the reaction mixture, and acidifying with 85% H_3PO_4. Extraction with ether removed all color from the aqueous layer. Separation of the ether layer and stripping gave material identical with the product which originally crystallized; combined weight of III, 1.25 g (98%). Recrystallization from absolute ethanol–ether raised the melting point 1° to 128–129°.

Its principal infrared bands were at 2.88, 7.39, 8.82, 8.93, 9.15, 9.96, 12.20, 13.31, and 14.29 μ.

Anal. Calcd for $C_{26}H_{26}FeO_2$: C, 73.28; H, 6.10; Fe, 13.11. Found: C, 73.23; H, 6.17; Fe, 13.81.

A solution of 0.380 g (1 mmole) of cyclic ether II was refluxed in 25 ml of ethanol containing 10 mmoles of sodium ethoxide. After 30 hr reflux was discontinued, water was added, and the solution was stripped to a dry powder. This was taken up in benzene and filtered and the filtrate was concentrated and chromatographed on alumina with benzene as eluent. A single fraction was obtained which was shown to be identical with starting material by melting point and superimposability of its infrared spectrum; recovery of II was 61%. Some decomposition of the ferrocene system appeared to have taken place.

B. Ring Opening of Cyclic Ether II.—A solution of 0.380 g (1 mmole) of II[2] was refluxed for 12 hr in a mixture of 20 ml of 95% ethanol and 10 ml of 4% aqueous acetic acid. At the end of this period the solvent system was stripped to an oil which crystallized. This was taken up in benzene and chromatographed on a microcolumn of alumina I. Elution with hexane–benzene gave a yellow powder, 0.30 g (70%), which after two recrystallizations from ether–95% ethanol gave III, mp 125–127.5° with an infrared spectrum superimposable on that of the product prepared in part A.

C. Treatment of Diol V with Aqueous Ethanolic Acetic Acid.—A murky solution of 0.25 g (0.63 mmole) of diol V[2] was refluxed in a mixture of 20 ml of 95% ethanol and 20 ml of 4% aqueous acetic acid for 7 hr. After this period the system was stripped, ether was added, and the resulting solution was washed with saturated Na_2CO_3 solution. The ether layer was separated, filtered, diluted with half its volume of ethanol, and stripped once again. The gummy solid formed was triturated with a

small amount of 95% ethanol; the yellow powder which resulted was isolated on a Büchner funnel and air dried. Recrystallization from absolute ethanol–ether afforded 1.9 g (71%) of carbinol ethyl ether III, mp 123–126°, with infrared spectrum superimposable on that of the product prepared by method A.

D. Treatment of Methiodide I with Aqueous Ethanolic Acetic Acid.—A slurry of 1.4 g (2.5 mmoles) of methiodide I[2] was refluxed in a mixture of 15 ml of 95% ethanol and 15 ml of 4% acetic acid. After 24 hr the system was stripped and the residue was extracted with ether. This solution was dried over $MgSO_4$, filtered, and stripped. Without further work-up, III was obtained, mp 123–126°, 0.78 g (81%), with infrared spectrum identical with that of the product prepared by method A.

E. Silver Oxide Method.—The methiodide I (0.57 g, 1 mmole) was dissolved in hot ethanol–water and shaken with excess Ag_2O (0.23 g, 2 mmoles) and filtered (ether wash), and the filtrate was concentrated on a rotary evaporator until an oil began to separate. Solid NaOH was added until a concentration of 50% was obtained. This solution was refluxed until no further trimethylamine was evolved (5 hr). The cooled solution was diluted with water and extracted with ether; the combined extracts were dried over $MgSO_4$. After stripping, 0.22 g (58%) of an orange, crystalline solid was obtained, mp 125–126°, from hexane. Repetition of this procedure on three times the scale described afforded 0.9 g (79%) of III, mp 127–128°, from ethanol, identical in all respects to the material prepared by method A.

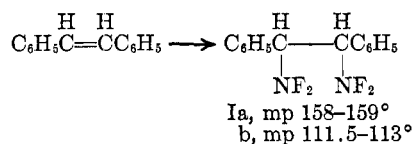## *meso-* and *dl-α,α′*-Bis(difluoramino)bibenzyls. Preparation and Nuclear Magnetic Resonance Spectra

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A recent study of the interaction of tetrafluorohydrazine (N_2F_4) and polycyclic aromatic hydrocarbons[1] included the report that *trans*-stilbene produced an *α,α′*-bis(difluoramino)bibenzyl. This addition compound of stilbene and N_2F_4 was reported to decompose above 80°, and was postulated from its proton nmr spectrum as either a mixture of *meso* and *dl* adducts or one adduct with two conformations.

As part of a study of the properties of organic difluoramino compounds, we have characterized the product from *trans*-stilbene and tetrafluorohydrazine[2] as a mixture of the *meso* and *dl* isomers. The *meso* isomer (Ia) was isolated in 37% yield; the *dl* isomer (Ib) was present in 50% yield.

$$C_6H_5C{=}CC_6H_5 \longrightarrow C_6H_5C{-}CC_6H_5$$

with H H above the left and H H above the right, and NF₂ NF₂ below

Ia, mp 158–159°
b, mp 111.5–113°

Addition of tetrafluorohydrazine to olefins appears to be a free-radical process,[2,3] and such a lack of stereospecificity is expected for radical additions to *trans*-stilbene.[4]

(1) H. Cerfontain, *J. Chem. Soc.*, 6602 (1965).

(2) R. C. Petry and J. P. Freeman, 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966, Abstract S-46.

(3) R. C. Petry and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 5912 (1961); A. J. Dijkstra, Ph.D. Thesis, Rotterdam, 1965.

(4) Addition of N_2O_4 to *trans*-stilbene, also a radical process: T. E. Stevens [*J. Am. Chem. Soc.*, **81**, 3593 (1959)] gave 21% *meso-α,α′*-dinitrobibenzyl and 32% *dl-α,α′*-dinitrobibenzyl.
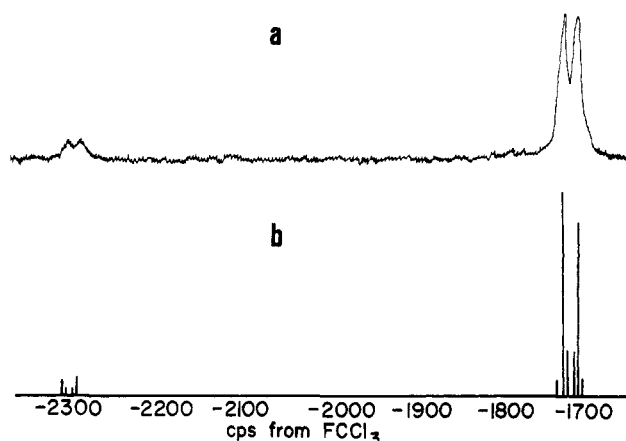
Figure 1.—(a) Observed F^{19} "B" spectrum; (b) calculated F^{19} "B" spectrum.

The nmr spectra of Ia and Ib are deceptively simple—only 18 peaks are apparent in the combined F^{19} and H^1 spectra of the *dl* mixture and even fewer for the *meso*. However, the line widths of the peaks (10–12 cps for F^{19} and 2–4 cps for H^1) make it obvious that these are not single transitions. Several reasons for this situation are discussed below.

Nitrogen coupling is not apparent in these compounds, although it has been observed at room temperature for NF_3, N_2F_4, and the N_2F_2 isomers. The nitrogen nucleus in the bibenzyl compounds is subject to a less symmetric environment, which may be expected to facilitate relaxation of this nucleus through a quadrupole mechanism. Cooling or warming of these compounds might be expected to either increase or decrease the visible effects of nitrogen on the F^{19} and H^1 spectra, but no noticeable changes occurred between -60 and $+100°$. However, decoupling of N^{14} by irradiation at 3.076 or 2.890 Mc for H^1 and F^{19} spectra, respectively, does cause a slight sharpening of peaks. Thus, while nitrogen (in part) accounts for the rather broad lines observed no spin–spin couplings to nitrogen influence the observed patterns.

The NF_2 groups are bound to optically active carbon atoms. The pyramidal geometry of the NF_2 group causes the two fluorine atoms to be magnetically nonequivalent in a fashion previously described[5] for CH_2 groups in similar environments. Significant shift differences for the two F^{19} nuclei result; acetone is a suitable solvent for the *dl* enantiomers in that it enhances the shift difference. Since each fluorine has a magnetically identical counterpart in the opposite enantiomer, spectra of the enantiomers are identical and indistinguishable. The F^{19} nmr (Figures 1 and 2) has the gross appearance of an ABX system of very large J_{FF} (587 cps) and comparatively small (10 to 30 cps) J_{HF_A} and J_{HF_B}.

The existence of an AB pattern from the C*–NF_2 system implies that the nitrogen atom is not inverting within the time characteristic of the nmr experiment. For only one nonring compound does this type of behavior appear to have been established[6]—the case of N-benzyl-O,N-dimethylhydroxylamine in the range of -30 to $-10°$. The AB spectrum of Ib was observed

(5) P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **47**, 49 (1961).

(6) D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965).