tion, an odor of piperidine was detected in the residue. Moistened indicator paper turned blue on contact with the residue, indicating that alcoholysis had occurred. Crystallization of phenylphosphonous dipiperidide from ethanol has been reported with no indication that alcoholysis occurs, except that the product possesses a piperidine-like odor.[3]

**Infrared Spectra of Ferrocenylphosphonous Dichloride and Ferrocenylphosphonous Dipiperidide.**—Infrared spectra were obtained from a liquid smear of the dichloride and from a Nujol mull of the dipiperidide, employing a Perkin-Elmer Model 321 spectrophotometer.

Both compounds show asymmetric ring breathing near 1110 cm.$^{-1}$, and in-plane C–H bending near 1005 cm.$^{-1}$,[12] which are characteristic of monosubstituted ferrocenes.[13] The compounds also show ferrocene C–H stretching and out-of-plane C–H bending bands in the regions 3060–3100 and 810–835 cm.$^{-1}$, respectively.[12] A C–C stretching band appears near 1410 cm.$^{-1}$,[12] in the spectrum of the dichloride, but is absent from this region in the spectrum of the dipiperidide. Both compounds absorb near 1310 and 1025 cm.$^{-1}$ in the regions assigned earlier[10] to the ferrocenylphosphorus group. Bands shown by the dichloride at 1164 and 1199 cm.$^{-1}$ and by the dipiperidide at 1150, 1160 (doublet), and 1212 cm.$^{-1}$ are due possibly to ferrocene in-plane C–H bending.[10,14] Other bands appear in the spectrum of the dipiperidide at 850, 890, 932, 1050, and 1115 (doublet with ferrocene band at 1108) cm.$^{-1}$. Bands attributable to P=O or P—O—H are not present in either spectra.

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[12] E. R. Lippincott and R. D. Nelson, *J. Am. Chem. Soc.*, **77**, 4990 (1955).

[13] M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5443 (1958).

[14] G. P. Sollott, H. E. Mertwoy, S. Portnoy, and J. L. Snead, *J. Org. Chem.*, **28**, 1090 (1963).

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# Dehydro-1,1′-trimethyleneferrocene[1]

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As part of a study of the chemistry of bridged ferrocenes we were led to examine the transformation of α-keto-1,1′-trimethyleneferrocene tosylhydrazone (2) under conditions of the Bamford–Stevens reaction.[2] This base-catalyzed reaction has been shown to give initially a diazo compound, which may undergo cationic decomposition in the presence of proton-donor solvents, or in their absence decompose to carbenic intermediates and thence products of hydrogen migration, skeletal rearrangement, or insertion reactions.[3] We were principally interested in the latter mode of this reaction since the action of carbenes on metallocenes has not been widely explored,[4] and the possibility existed that an insertion reaction might lead to a cyclopropane-bridged ferrocene.

The tosylhydrazone (2) was readily prepared from the bridged ketone (1) by treatment with toluenesulfonylhydrazine under normal reaction conditions. Irradiation of 2 in dimethoxyethane solution in the presence of sodium methoxide failed to give any well-defined products. When decomposition was carried out thermally in dimethoxyethane solution with sodium methoxide, the products were α-methoxy-1,1′-trimethyleneferrocene and the ketone (1), while with dimethyl sulfoxide as solvent 1,1′-trimethyleneferrocene (4) in addition to 1 was isolated. However, when the tosylhydrazone was subjected to thermal decomposition in cyclohexane solution in the presence of sodium methoxide or preferably sodium hydride, moderate yields of dehydro-1,1′-trimethyleneferrocene (3) were obtained. The structural assignment for this substance is supported by its elemental analysis and by its n.m.r. spectrum (peaks at τ 3.96, 6.05, and 7.23, relative intensity 2:8:2),[5] and is confirmed by its conversion to 4 on catalytic hydrogenation. The new compound is the simplest member of a class of ferrocene derivatives possessing an unsaturated three-carbon bridge linking the two rings.[6]

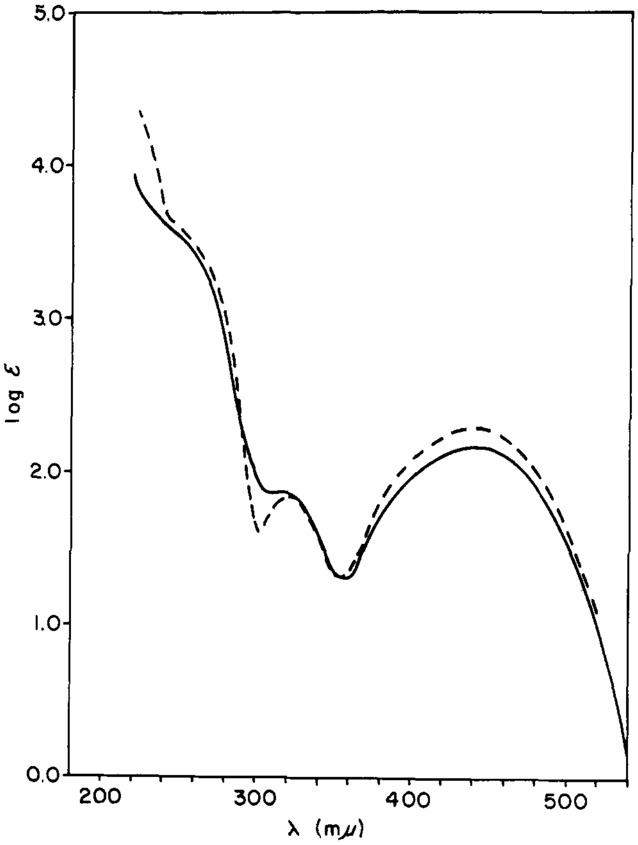

Fig. 1.—Ultraviolet and visible absorption spectra, taken in 95% ethanol: ......, 1,1′-trimethyleneferrocene (4); ———, dehydro-1,1′-trimethyleneferrocene (3).

Although the aprotic reaction conditions under which 3 is produced are those favoring the generation of a carbenoid intermediate, no products such as 5 or 6, which might be expected to be formed from such an intermediate, were detected. In this respect the reaction of 2 more closely resembles the behavior of cyclohexanone and cyclopentanone tosylhydrazones

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[1] This research was supported by a grant (RG-5978) from the National Institutes of Health, U. S. Public Health Service.

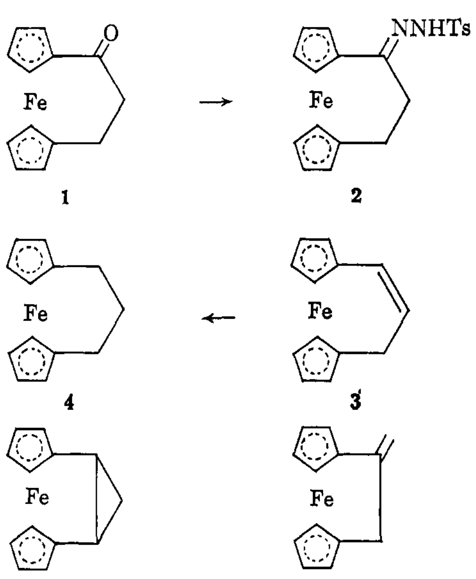
[2] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

[3] (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **82**, 1002 (1960). (b) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959). (c) P. Clarke, M. C. Whiting, G. Papenmeier, and W. Reusch, *J. Org. Chem.*, **27**, 3356 (1962).

[4] J. H. Richards, K. Plesske, and H. Werner, Abstracts, Symposium on Current Trends in Organometallic Chemistry, University of Cincinnati, Cincinnati, Ohio, June, 1963, p. 77.

[5] Determined in $CDCl_3$ solution at a concentration of approximately 60 mg./ml. and recorded at 60 Mc. with a Varian Model V-4300 spectrometer. Peak positions were calibrated against tetramethylsilane as internal standard by side banding.

[6] For other such compounds, *cf.* M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish, and V. Schlatter, *J. Am. Chem. Soc.*, **85**, 316 (1963); W. Mock and J. H. Richards, *J. Org. Chem.*, **27**, 4050 (1962). K. L. Rinehart, *et al.* [*J. Am. Chem. Soc.*, **84**, 3263 (1962)] had earlier attempted, without success, to prepare dehydro-1,1′-trimethyleneferrocene by dehydration of α-hydroxy-1,1′-trimethyleneferrocene.



than of the corresponding acyclic or small ring carbonyl derivatives which give appreciable amounts of products derived from carbenoid insertion and rearrangement processes.[3a] The possibility that **5** is formed in the reaction, but is rearranged to **3** during chromatographic resolution of the reaction mixture may not, however, be excluded.

A comparison of the ultraviolet spectrum of **3** with that of **4** (Fig. 1) provides a particularly striking demonstration of the absence of conjugation between the ethylenic bond and the cyclopentadienyl ring in **3**.

## Experimental

**α-Keto-1,1′-trimethyleneferrocene *p*-Toluenesulfonylhydrazone** (**2**).—A solution of 240 mg. (1.0 mmole) of the ketone and 190 mg. (1.0 mmole) of *p*-toluenesulfonylhydrazine in 30 ml. of ethanol containing a few drops of acetic acid was heated on the steam bath for 0.5 hr. On cooling, the hydrazone separated as lustrous golden rods, m.p. 198.5–200.0°, with darkening, yielding 337 mg. (82%). An analytical sample (from ethanol) melted at 201–202°.

*Anal.* Calcd. for $C_{20}H_{20}FeN_2O_2S$: C, 58.83; H, 4.94; N, 6.86. Found: C, 58.90; H, 4.83; N, 7.02.

**Dehydro-1,1′-trimethyleneferrocene** (**3**).—Sodium hydride (180 mg., 7.5 mmoles) was added to a solution of 500 mg. of the tosylhydrazone (1.2 mmoles) in 50 ml. of cyclohexane. The solution was heated at reflux, in an atmosphere of nitrogen, for 12 hr., then cooled, poured into water, and extracted with ether. The combined ether–cyclohexane extract was washed to neutrality and dried over magnesium sulfate. Removal of solvent left a crude crystalline product which was taken up in Skellysolve B and chromatographed on an alumina column. Three bands appeared. The first gave 45 mg. (22%) of **3**, m.p. 100.5–102.5°, after further chromatographic purification followed by sublimation.

The second band afforded 19 mg. of α-keto-1,1′-trimethyleneferrocene (**1**), and the third 120 mg. of starting material. With sodium methoxide as base **3** was obtained in 14% yield.

*Anal.* Calcd. for $C_{13}H_{12}Fe$: C, 69.68; H, 5.40. Found: C, 70.05; H, 5.28.

**Reduction of Dehydro-1,1′-trimethyleneferrocene.**—The olefin (25 mg., 0.1 mmole) was taken up in 10 ml. of methanol and hydrogenated at atmospheric pressure and room temperature in the presence of platinum oxide catalyst. At the end of 36 hr., the catalyst was filtered off, solvent was removed, and the product was chromatographed on a short alumina column using Skellysolve B as eluent. In this manner, 11.4 mg. of 1,1′-trimethyleneferrocene, m.p. 100.5–104.0°, was obtained. Its infrared spectrum was identical with that of an authentic sample, and its mixture melting point with a sample of **4** (m.p. 107.5–108.5°) was 105–106°.

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# A New Phenothiazine Synthesis. The Halogen-Induced Smiles Rearrangement[1]

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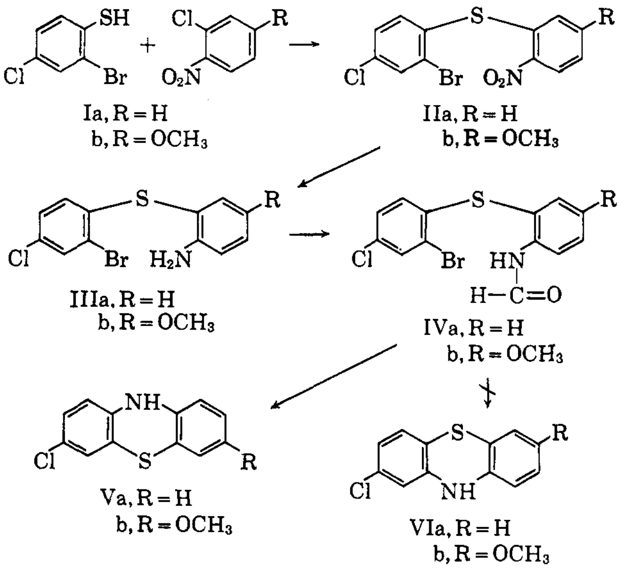
*Received March 10, 1964*

Bonvicino, Yogodzinski, and Hardy have reported a new Smiles-type rearrangement in which bromo replaces nitro as the activating group.[2] They encountered this rearrangement in the synthesis of phenoxazines by dehydrohalogenation of *o*-bromo-*o*′-alkylaminodiphenyl ethers in benzene in the presence of sodamide. Bonvicino, *et al.*, considered the possibility that the same rearrangement could take place with potassium carbonate in N,N-dimethylformamide (DMF), but they minimized this possibility on theoretical grounds.

Our work on the preparation of the isosteric phenothiazines by dehydrohalogenation of *o*-bromo-*o*′-formamidodiphenyl sulfides (IVa and IVb) has shown that the halogen-induced Smiles rearrangement can indeed take place in DMF–potassium carbonate.

The intermediates (IVa and IVb) were prepared by the routine reaction sequence[3] outlined in Scheme I.

SCHEME I



Cyclizations of IVa and IVb were effected by heating under reflux, in N,N-dimethylformamide, in the presence of anhydrous potassium carbonate and copper–bronze catalyst. Instead of the anticipated 2-chlorophenothiazine (VIa, m.p. 198.5–199.5°)[4-6] and 2-

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[1] This rearrangement was first described in our Sixth Progress Report (April 30, 1963) to the Psychopharmacology Service Center, National Institute of Mental Health, Bethesda, Md., under Contract SA-43-ph-3758.

[2] G. E. Bonvicino, L. H. Yogodzinski, and R. A. Hardy, Jr., *J. Org. Chem.*, **27**, 4272 (1962).

[3] E. A. Nodiff, S. Lipschutz, P. N. Craig, and M. Gordon, *ibid.* **25**, 60 (1960).

[4] P. Charpentier, P. Gaillot, R. Jacob, J. Gaudechon, and P. Buisson, *Compt. rend.*, **235**, 59 (1952).

[5] H. L. Yale, *J. Am. Chem. Soc.*, **77**, 2270 (1955).

[6] We are grateful to Dr. Paul N. Craig of Smith Kline and French Laboratories, Philadelphia, Pa., for samples of 2-chloro- and 3-chlorophenothiazine.