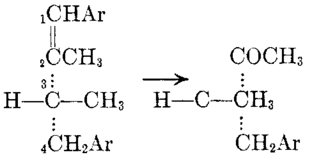
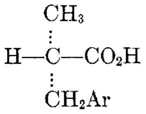
Hydroxylation of II with osmium tetroxide,[7] periodate oxidation of the oily diol, and treatment with Girard's reagent P gave 4-(3,4-dimethoxyphenyl)-3-methyl-2-butanone (III), isolated as the semicarbazone (75% yield from II), m.p. 158.7–159.3°, $[\alpha]^{20}_{D}$ −48.0° (chloroform) (Found: C, 60.05; H, 7.57; N, 15.08). (+)-3,4-Dimethoxy-α-methylhydrocinnamic acid (IV), b.p.$_{0.01}$ 130° (bath temperature), $[\alpha]^{21}_{D}$ +27.5° (chloroform) (Found: C, 63.84; H, 7.16), obtained by resolving the racemate[8] with quinine, was converted with oxalyl chloride to the chloride, b.p.$_{0.015}$ 90° (bath temperature), $[\alpha]^{20}_{D}$ +20.5° (benzene), which with ethereal methylmagnesium bromide at −74° afforded the optical antipode of III, again isolated as the semicarbazone (17% yield[9]), m.p. 156.5–157.5°, $[\alpha]^{21}_{D}$ +46.7° (chloroform).



$$\begin{array}{c}{}_{1}\mathrm{CHAr}\\ \| \\ {}_{2}\mathrm{CCH_3}\\ {}_{3}\vdots\\ \mathrm{H{-}C{-}CH_3}\\ \vdots\\ {}_{4}\mathrm{CH_2Ar}\end{array} \longrightarrow \begin{array}{c}\mathrm{COCH_3}\\ \vdots\\ \mathrm{H{-}C{-}CH_3}\\ \vdots\\ \mathrm{CH_2Ar}\end{array}$$

II III

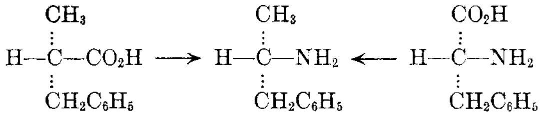


$$\begin{array}{c}\mathrm{CH_3}\\ \vdots\\ \mathrm{H{-}C{-}CO_2H}\\ \vdots\\ \mathrm{CH_2Ar}\end{array}$$

Ar = 3,4-$(MeO)_2C_6H_3$

IV

IV and (+)-α-methylhydrocinnamic acid (V), $[\alpha]_D$ +27.7° (chloroform),[10] have identical rotations; hence they most certainly[11] belong to the same configurational series. Curtius degradation of V[12] gave (+)-α-methylphenethylamine (VI), identical in rotatory sign with the product obtained from D-phenylalanine (VII) by Karrer and Ehrhardt.[13] It follows that II possesses the D-configuration and that I is 1D, 2L, 3D, 4D.[14] These findings also indicate the absolute configurations of other lignans, insofar as they have been previously correlated[3,15] with I or II.



$$\begin{array}{c}\mathrm{CH_3}\\ \vdots\\ \mathrm{H{-}C{-}CO_2H}\\ \vdots\\ \mathrm{CH_2C_6H_5}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH_3}\\ \vdots\\ \mathrm{H{-}C{-}NH_2}\\ \vdots\\ \mathrm{CH_2C_6H_5}\end{array} \longleftarrow \begin{array}{c}\mathrm{CO_2H}\\ \vdots\\ \mathrm{H{-}C{-}NH_2}\\ \vdots\\ \mathrm{CH_2C_6H_5}\end{array}$$

V VI VII

We are greatly indebted to Dr. W. Klyne for very stimulating discussions and extremely helpful suggestions. Miss Mary M. Trail performed a large portion of the experimental procedures.

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(7) Criegee, Marchand, and Wannowius, *Ann.*, **550**, 99 (1942).

(8) Haworth, Mavin, and Sheldrick, *J. Chem. Soc.*, 1423 (1934).

(9) Dimethylcadmium yielded 46% partly racemized semicarbazone, m.p. 155–156°, $[\alpha]^{21}_{D}$ +36°.

(10) Pickard and Yates, *J. Chem. Soc.*, **95**, 1011 (1909); *cf.* Kipping and Hunter, *J. Chem. Soc.*, **83**, 1005 (1903).

(11) See Klyne, ref. 6, pp. 204 and 78, respectively.

(12) Jones and Wallis, *J. Am. Chem. Soc.*, **48**, 169 (1926); *cf.* Wallis and Nagel, *J. Am. Chem. Soc.*, **53**, 2787 (1931).

(13) Karrer and Ehrhardt, *Helv. Chim. Acta*, **34**, 2202 (1951); *cf.* Leithe, *Ber.*, **65**, 660 (1932).

(14) *Cf.* Klyne, *Chemistry & Industry*, 1022 (1951). These assignments also agree with the McCasland system ("*A New General System for the Naming of Stereoisomers*," *Chemical Abstracts*, Columbus, Ohio, 1953), according to which I is expressed as D(1,3,4)A.

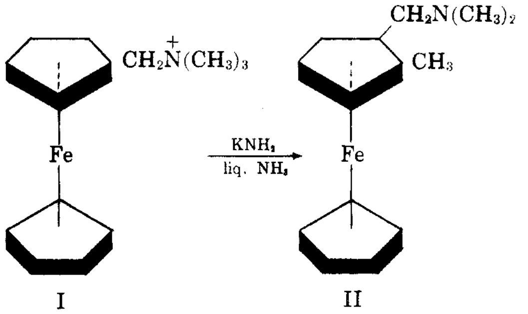
(15) Including the diarylbutanes, lariciresinol, pinoresinol, conidendrin, the peltatins; *cf.* Hartwell, Schrecker, Leiter, and Shilling, *Abstracts of Papers, Am. Chem. Soc.*, 125th Meeting, 11M (1954).

(16) National Institutes of Health, Public Health Service, U. S. Department of Health, Education, and Welfare.

Ortho Substitution Type of Rearrangement with Quaternary Ammonium Ions of Dicyclopentadienyliron by Potassium Amide[1]

Sir:

We have simulated the *ortho* substitution type of rearrangement of the benzyltrimethylammonium ion[2] with the ferrocenyltrimethylammonium ion[3] (I) which gave the 2-methyl derivative (II). This appears to be the first example of an aromatic nucleophylic type of reaction with such an iron compound.



I II

Quaternary ammonium ion I (as the iodide) gave, with potassium amide in liquid ammonia (two hours), a 60% yield of *tertiary amine II*, b.p.

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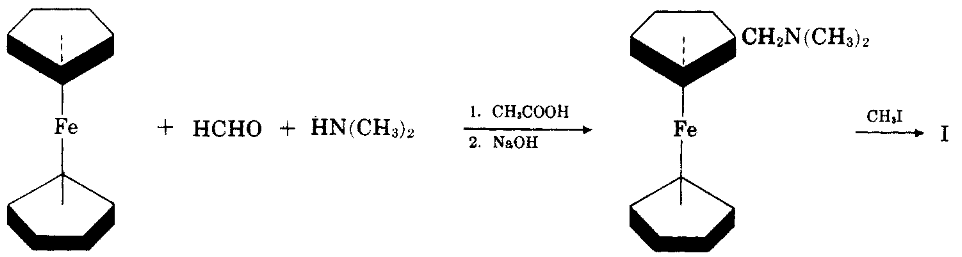
(1) This work was supported by the Office of Ordnance Research, U. S. Army.

(2) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

(3) The more common electrophilic aromatic character of ferrocene has been noted by Woodward, Rosenblum, and Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).



III

IV

101–103° at 0.3 mm. *Anal.*[4] Calc'd for $C_{14}H_{19}FeN$: C, 65.38; H, 7.45; N, 5.45. Found: C, 65.16; H, 7.40; N, 5.74. The *picrate* (green-yellow plates) melted at 179–180° dec. *Anal.*[4] Calc'd for $C_{20}H_{22}FeN_4O_7$: C, 49.40; H, 4.56; N, 11.52; Fe, 11.49. Found: C, 49.48; H, 4.55; N, 11.48; Fe, 11.62.

The starting point for the present work was ferrocene (III) (dicyclopentadienyliron)[5] which was converted to tertiary amine (IV) essentially as described by Schmidle and Mansfield[6] for the corresponding reaction with methylstyrene.

Tertiary amine (*IV*), b.p. 91–92° at 0.45 mm., was obtained in 51% yield. *Anal.*[4] Calc'd for $C_{13}H_{17}FeN$: C, 64.22; H, 7.05; N, 5.76. Found: C, 64.46; H, 6.83; N, 5.85. The *picrate* (red needles) melted at 162–163° dec. *Anal.*[4] Calc'd for $C_{19}H_{20}FeN_4O_7$: C, 48.32; H, 4.27; N, 11.86; Fe, 11.83. Found: C, 48.22; H, 4.51; N, 11.81; Fe, 11.57.

Tertiary amine (IV) was methylated with methyl iodide to give in 95% yield the *quaternaryammonium iodide of I* (yellow crystals), which decomposed slowly at 220°. *Anal.*[4] Calc'd for $C_{14}H_{20}FeIN$: C, 43.66; H, 5.24; N, 3.64; Fe, 14.50. Found: C, 43.50; H, 5.26; N, 3.76; Fe, 14.24.

A more complete study of these and related reactions is being carried out.

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[4] Analysis by Galbraith Laboratories, Knoxville, Tennessee.

[5] We are indebted to Dr. R. L. Pruett of Linde Air Products, Tonawanda, N. Y., for a generous sample of this compound.

[6] C. J. Schmidle and R. C. Mansfield, *J. Am. Chem. Soc.*, **77**, 4636 (1955).