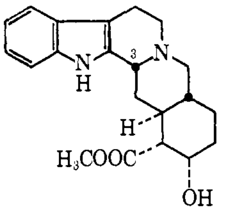
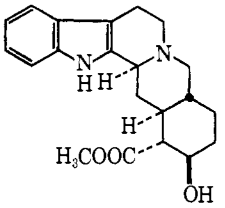
in methanol) to produce **9**, mp 143–144°, from acetonitrile (acetate mp 167–169°, nmr δ 5.43, J = 7 Hz).

The synthesis of yohimbine was completed by regiospecific cyclization, effected by heating the seco alcohol **9** with 2 equiv of mercuric acetate–ethylenediaminetetraacetic acid disodium salt (EDTA)[10] (1:1) at 125° for 2 hr in aqueous 1% acetic acid, followed by reduction of the crude intermediate with sodium borohydride (1 equiv, 0°, 15 min in methanol). (±)-Yohimbine (**2**) was thus obtained in ~32% yield from **9** as the only isolatable product (mp 214–216° from methanol, lit.[2b] mp 218–220°). The nmr, ir, and mass spectra (m/e 354.1947) were indistinguishable from those of the natural substance.

The stereoselective route to yohimbine which has just been described can be modified to lead to (±)-ψ-yohimbine (**11**) or to (±)-β-yohimbine (**12**).



11



12

Treatment of **9** with 10 equiv of mercuric acetate in aqueous 5% acetic acid at 120° for 3.5 hr, followed by removal of mercury salts and interfering by-products (with hydrogen sulfide, and then sodium borohydride in methanol for 15 min at 0°), gave (±)-ψ-yohimbine (**11**), mp 248–251° (from methanol; lit.[2a] mp 252–256°) in 27% yield.[11] No yohimbine appeared to be produced under these conditions.[12]

The synthesis of β-yohimbine (**12**) was effected simply by cleavage of **3** with cyanogen bromide, followed by reduction with sodium borohydride in methanol. The mixture of the N-cyano alcohols **5** and **6** was now predominantly the equatorial isomer **6** (**5**:**6** = 11:89) which was easily separated to give pure **6** (*vide supra*), mp 152–153.5°. Removal of the cyano group and alkylation with trytophyl bromide were performed as described above for the epimeric **5**, leading successively to **8**, mp 153–155° (65%, ir 3120 cm^{-1}), and **10**, mp 78–84° (acetate mp 153–154°, nmr δ 4.98, J = 21 Hz). The latter was finally cyclized (as described above for (±)-yohimbine) to (±)-β-yohimbine (**12**), mp 132–137 and 227–232°[2b] (lit. mp 130–140 and 232–236°) in 31% yield.[11,13]

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[10] Only 2 equiv of mercuric acetate is required since mercury, rather than mercurous acetate, is produced in the presence of EDTA; *cf.* J. Knabe and H. P. Herbort, *Arch. Pharm.*, **300**, 774 (1967). Closely related observations in another series have appeared since the completion of our work (*cf.* J. Gutzwiller, G. Pizzolato, and S. M. Uskokovic, *J. Amer. Chem. Soc.*, **93**, 5907 (1971)).

[11] The ir, nmr, and mass spectra of the synthetic (±) material were identical with those of an authentic sample of the natural substance. We thank Professor E. Wenkert (Indiana) and Dr. R. A. Lucas (Ciba) for samples of natural ψ- and β-yohimbine, respectively.

[12] The oxidation of **9** by mercuric acetate with and without EDTA gives strikingly different results. The kinetic formation of the ψ stereochemistry at C_3 is not unexpected (*cf.* ref 2a) while the stability of the resulting ψ-yohimbine to oxidation by mercuric acetate either alone (F. L. Weisenborn and P. A. Diassi, *J. Amer. Chem. Soc.*, **78**, 2022 (1956); E. Wenkert and D. K. Roychaudhuri, *J. Org. Chem.*, **21**, 1315 (1956)), or in the presence of EDTA at 70° (L. Bartlett, N. J. Dastoor, J. Hrbek, Jr., W. Klyne, H. Schmid, and G. Snatzke, *Helv. Chim. Acta*, **54**, 1238 (1971)), is well documented. The implication of our work on the transformation of **9** to yohimbine is that at 120° in the presence of EDTA, the kinetically produced ψ-yohimbine must be oxidized to the iminium salt, which then gives the expected yohimbine stereochemistry at C_3 on borohydride reduction. We indeed were able to show that (±)-ψ-yohimbine could be oxidized with mercuric acetate–EDTA under more rigorous conditions (120°, 3 hr) than described by Bartlett, *et al.* (*vide supra*), to an intermediate (which was then reduced with sodium borohydride) to (±)-yohimbine in 41% overall yield.

[13] We thank the National Science Foundation and the National Institutes of Health for their support of this work.

Gilbert Stork,* R. Nath Guthikonda
Department of Chemistry, Columbia University
New York, New York 10027

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Semiconducting Polymers. Mixed Valence Ferrocene–Ferricenium Polymers[1]

Sir:

The mixed valence compound, biferrocene [Fe(II)-Fe(III)] picrate (**1**) exhibits properties which are not the sum of the properties of ferrocene and ferricenium picrate.[2] The single-crystal conductivity of **1** was six orders of magnitude greater than either of its components, and a new electronic transition (1900 nm), ascribed to an electron-transfer band, was observed for **1**. We proposed that it should be possible to alter the electrical properties of ferrocene polymers by the partial oxidation of these compounds.[2] Recently several ferrocene–ferricenium polymers have been prepared and characterized,[3,4] and we now report on the electrical properties of three structurally different mixed valence ferrocene polymers.

Poly(vinylferrocene) (**2**),[3,5] ferrocene-*o*-anisaldehyde condensation polymer **3**,[6] and polyferrocenylene (**4**)[7,8] were prepared by published methods and then oxidized with benzoquinone, HBF_4, and also with 2,3-dichloro-5,6-dicyanoquinone (DDQ) and 3,4,5,6-tetrachloro-1,2-benzoquinone (*o*-CA). The oxidized polymers **5**–**7** were blue-green or black in color due to the ferricenium 620-nm ${}^2E_{2g} \rightarrow {}^2E_{1u}$ transition. No absorption in the 1900-nm region was observed for **5** and **6** but a weak long wavelength transition was observed for **7**. For every mole of DDQ, *o*-CA, or BF_4^- incorporated into the polymers, 1 mol of ferrocene units was oxidized. This could be rigorously established by the comparison of the elemental analysis and the Fe(II)/Fe(III) ratio determined by infrared,[3] Mössbauer,[3,9] and X-ray photoelectron spectroscopy[10] studies as described previously.

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[1] The Organic Solid State. VII. For part VI see D. O. Cowan J. Park, M. Barber, and P. Swift, *Chem. Commun.*, 1444 (1971). Also, Organometallic Polymers. XVII. For part XVI, see C. U. Pittman, Jr., T. L. Grube, O. E. Ayers, S. T. McManus, M. D. Rausch, and G. A. Mosher, *J. Polym. Sci., Part A-1*, **10**, 379 (1972).

[2] D. O. Cowan and F. Kaufman, *J. Amer. Chem. Soc.*, **92**, 219 (1970); F. Kaufman and D. O. Cowan, *ibid.*, **92**, 6198 (1970).

[3] C. U. Pittman, Jr., J. C. Lai, T. D. Rounsefell, D. Vanderpool, M. Good, and R. Prados, *Macromolecules*, **3**, 746 (1970); C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, and R. Prados in "Polymer Characterization: Interdisciplinary Approaches," C. D. Carver, Ed., Plenum Press, New York, N. Y., 1971.

[4] C. U. Pittman, Jr., *Chem. Technol.*, **1**, 416 (1971).

[5] F. S. Arimoto and A. C. Haven, *J. Amer. Chem. Soc.*, 77, 6295 (1955).

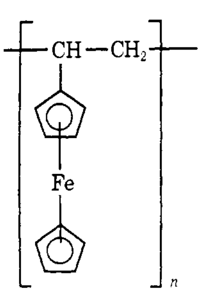
[6] E. W. Neuse and K. Koda, *J. Organometal. Chem.*, 4, 475 (1965).

[7] Samples of **4** were prepared by the polyrecombination technique (ref 8). Additionally, several samples were generously provided by Dr. N. Bilow, Hughes Aircraft Corp., Culver City, Calif.

[8] N. Bilow, A. L. Landis, and H. Rosenberg, *J. Polym. Sci., Part A-1*, 7, 2719 (1969).

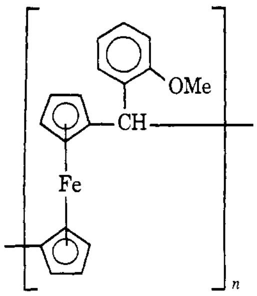
[9] D. O. Cowan, R. L. Collins, and F. Kaufman, *J. Phys. Chem.*, **75**, 2025 (1971).

[10] D. O. Cowan and J. Park, *Chem. Commun.*, 1444 (1971).



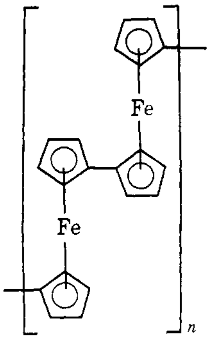
2

5 (a fraction of Fe in **2** oxidized)



3

6 (a fraction of Fe in **3** oxidized)



4

7 (a fraction of Fe in **4** oxidized)

The dc electrical conductivity measurements were performed on compressed pellets (~0.5-g samples) either spring loaded between polished stainless steel electrodes corresponding to the surface area of the pellets or by using the silver conducting epoxy electrode technique described earlier.[2] No noticeable change in conductivity was detected for any of the compounds even after prolonged passage of current. This indicates that the conduction mechanism was electronic and not ionic. The conductivity of pure **2** was 8 × $10^{-12}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

Upon oxidation to **5** with DDQ, the conductivity increased to 2 × $10^{-8}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ when 68% of the rings were converted to ferricenium moieties. Similar conductivity enhancements were observed when BF_4^- and *o*-CA·⁻ were the anions in polysalts **5** (*i.e.*, 3 × $10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ when $X^- = BF_4^-$, 76% oxidation and 5 × $10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ when X^- = *o*-CA·⁻, 62% oxidation). The presence of the π system and unpaired spin density in the anions, DDQ·⁻ and *o*-CA·⁻, does not cause any marked increase in the conductivity of **5**. Thus, the conductivity of **5** seems to be insensitive to the counterion structure. This has not yet been established for **7**.

Table I summarizes representative data from oxidation–conductivity studies on *o*-anisaldehyde–ferrocene polymer **3** as a function of the Fe(II)/Fe(III) ratio. A maximum conductivity for the polysalt of **3** is observed when more than 70% of the ferrocene moieties are oxidized. This observation is consistent with optimal electrical conductivity arising from an electron hopping model[11] where ferrocene is surrounded by all nearest-neighbor ferricenium moieties.

Table I. Ferrocene–*o*-Anisaldehyde Polymer

% Fe oxidized	C, %	H, %	σ, $\Omega^{-1}\ \mathrm{cm}^{-1}$ [a]	Preparation[b] (% yield)
0[c]	70.09	5.32	5 × 10^{-12}	
59[d]	60.70	4.81	6 × 10^{-8}	1P:$^1/_8$BQ:$^1/_4$$HBF_4$ (8)
68[d]	59.36	4.45	2 × 10^{-7}	1P:$^1/_4$BQ:$^1/_2$$HBF_4$ (24)
73[d]	58.66	4.50	2 × 10^{-6}	1P:$^1/_2$BQ:2HBF_4 (83)
98[d]	55.35	4.30	5 × 10^{-8}	1P:$^1/_2$BQ:10HBF_4 (89)

[a] Average of more than ten measurements at 21°. [b] Ratio of reagents in the synthesis of the oxidized polymer, P = polymer, BQ = benzoquinone, and HBF_4. The solvent in all cases was THF. [c] Calculated for **3**: C, 70.76; H, 5.31; mol wt, 3600. [d] Calculated from the C and H analysis of the fluoroborate salt.

Table II. Polyferrocenylene Polysalt Conductivity Measurements[a]

Oxidizing agent, X	% Fe oxidized	Conductivity at 25°, $\Omega^{-1}\ \mathrm{cm}^{-1}$	Thermal activation energy, eV
Pure (none)[b]	0	6.4 × 10^{-14}	0.62 (rt–65°)[c]
	~1–3[b]	2.41 × 10^{-12}	0.60 (rt–65°)
			0.35 (65–100°)
DDQ	50	5.85 × 10^{-10}	0.49 (rt–100°)
DDQ	60	4.15 × 10^{-11}	0.50 (rt–100°)
o-CA	80	3.96 × 10^{-10}	0.48 (rt–100°)

[a] Number averaged molecular weight 2200; the repeating units shown as **4** and **7** are idealized since alkyl side chains are present and the average repeating unit weight is 215. The same polyferrocenylene sample was used for all these studies. [b] After preparation by the polyrecombination technique some oxidized Fe units remain after work-up. The amount was estimated by uv measurements. After treatment with Ce^{2+} and thorough repurification only ferrocene units could be detected. [c] rt = room temperature.

Table II lists results from conductivity studies on polyferrocenylene (**4**) and its polysalts **7**. Again the introduction of mixed valence states sharply increases the conductivity and decreases the thermal activation energy. Upon irradiation with a 200-W tungsten lamp, no increase in the dark conductivity of **4** or **7** was found. This is a particularly interesting compound for study because of the possible direct π conjugation of the ferrocene–ferricenium units. The preferred conformation of biferrocene is the "staggered" structure shown for polyferrocenylene in **4**.[12] This conformation and others, where the planes of the ferrocene rings are rotated to various small dihedral angles, probably predominate in polymers **4** and **7** because the "eclipsed" conformation would have serious nonbonded hydrogen repulsions. In the staggered conformation there should be maximum π conjugation; as the rings are rotated through small angles the interaction will be proportional to the cosine of the angle. However, magnetic susceptibility,[13] Mössbauer,[3,9] and uv[2,14] studies indicate that in ferricenium salts and in mixed valence salts of biferrocene and polyferrocenylene, the positive charge is largely localized at the iron atom. No appreciable delocalization, *via* the cyclopentadiene rings, to adjacent ferrocene units exists. Thus, electron transfer through the π system is rendered unlikely and the electron-hopping model, with such "conjugative" assistance in **7**, seems to be no more effective in **7** than it is in **5** where conjugation is impossible.

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(11) E. Gutmann and L. E. Lyons, "Organic Semiconductors," Wiley, New York, N. Y., 1967.

(12) A. C. MacDonald and J. Trotter, *Acta Crystallogr.*, 17, 872 (1964).

(13) D. O. Cowan, G. A. Candela, and F. Kaufman, *J. Amer. Chem. Soc.*, 93, 3889 (1971).

(14) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *ibid.*, 92, 3234 (1970); 93, 3603 (1971).

A simple electron-hopping model for the electrical conductivity is consistent with the observations that the conductivity is relatively insensitive to the anion structure, or to conjugation, but is very sensitive to the fraction of the ferrocene units oxidized.

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Dwaine O. Cowan,* J. Park
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Charles U. Pittman, Jr., Yukihiko Sasaki
Department of Chemistry, The University of Alabama
University, Alabama 35486

Tapan K. Mukherjee, Noreen A. Diamond
Energetics Branch, Air Force Cambridge Research Laboratories
Bedford, Massachusetts 01730

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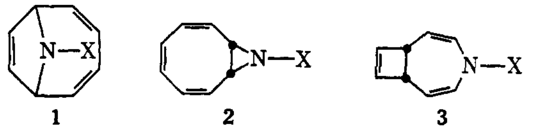
New Routes to 9-Azabicyclo[4.2.1]nona-2,4,7-trienes. On the Rearrangement of 9-Azabicyclo[6.1.0]nona-2,4,6-trienes

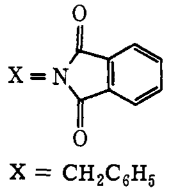
Sir:

Carbanions are known to react with alkyl nitrites to afford oximes which are convertible to carbonyl compounds.[1] The reaction between dipotassium cyclooctatetraenide (COT^{2-})[2] and isoamyl nitrite in THF could give the bisoxime of cyclooctatetraenequinone, but instead the reaction leads by formal 1,4 bridging[3] to **1a** (74%, mp 112.0–112.5°). This result is most useful anyway because the bridged hydroxylamine (**1a**) represents an efficient, new entry into the 9-azabicyclo[4.2.1]nona-2,4,7-triene ring system **1**.[4] The ready availability of **1a** has allowed an examination of its chemistry and the results have proven to be both synthetically useful and interesting. We report on these results and on still another approach to ring system **1** through valence isomerization of a bicyclo[6.1.0]nonatriene (**2**).



1 **2** **3**

a, X = OH
b, X = H
c, X = $COOCH_3$
d, X = CN
e, X = NH_2

f, X =


g, X = $CH_2C_6H_5$
h, X = CH_3
i, X = +

Zinc–acetic acid reduction of **1a** affords the parent amine **1b** (95% crude, 61% after flash distillation); reaction of **1b** with methyl chloroformate affords **1c** (75%, mp 51.0–52.5°) and with cyanogen bromide gives **1d** (47%, mp 96.0–97.5°). The latter, the only previously known derivative of **1**, was prepared earlier by Anastassiou in 3.4% yield by reacting cyanogen azide with cyclooctatetraene.[4]

It is interesting that the reaction between COT^{2-} and isoamyl nitrite produces **1a** but not **2a** or **3a**. In earlier work, the urethane **2c** (ethyl ester) was observed to rearrange quantitatively to **3c** (80°, 30 min)[5] and not to **1c**. The previously reported cyanamide **2d** appeared not to rearrange thermally to either **1d** or **3d**.[4] Thus, at first glance it would appear that **1a** results from the direct (presumably in several steps) 1,4 addition of the alkyl nitrite to COT^{2-} and not by initial 1,2 addition followed by rearrangement.[2b,3] Additionally, we have been unable to detect the presence of any skeletal isomer which rearranges to **1a** in the reaction. However, we now report an example of just such a **2** → **1** transformation and this example provides yet another synthetic entry into ring system **1**.[6]

Lead tetraacetate oxidation of *N*-aminophthalimide in the presence of a tenfold excess of cyclooctatetraene in dichloromethane[7] affords a substance identified as **2f** (42%, mp 180.5–182.0°) [nmr ($CDCl_3$) τ 2.1–2.4 (4 H, m, aromatic), 3.3–4.2 (6 H, m, olefinic), and 6.81 (2 H, s, allylic);[8] uv (95% ethanol) λ_{max} 237 nm (ϵ 33,600); ir (KBr) 1697 cm^{-1} C=O)]. Hydrolysis (NaOH and then concentrated HCl) of **2f** afforded, after preparative vpc purification, a 20% yield of **1e** (colorless oil). The hydrazine **1e** was identified by comparison of its spectral characteristics with those of related bicyclo[4.2.1]nonatrienes described herein and by its independent synthesis from **1b**. The parent amine **1b** was allowed to react with hydroxylamine-*O*-sulfonic acid–KOH to afford a low yield (1.1% after purification) of **1e** which proved identical (nmr, ir, vpc) with the material prepared from **2f**. The hydrazine **1e** is best prepared from **2f**.

The hydrolysis of **2f** to **1e** was also effected with excess hydrazine in ethanol (1 hr) but the yield was lower. When **2f** was treated with excess hydrazine at room temperature for 3 min, examination of the crude mixture by nmr revealed the presence of small amounts of **1e**. We have been unable to detect the presence of **2e**. Com-

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(1) (a) C. H. DePuy and B. W. Ponder, *J. Amer. Chem. Soc.*, **81**, 4629 (1959); (b) E. H. Timms and E. Wildsmith, *Tetrahedron Lett.*, 195 (1971).

(2) (a) E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965); (b) see also, T. J. Katz, C. R. Nicholson, and C. A. Reilly, *ibid.*, **88**, 3832 (1966).

(3) Acylation of COT^{2-} affords mixtures of 1,2 and 1,4 adducts [T. S. Cantrell and H. Shechter, *ibid.*, **89**, 5868 (1967); **85**, 3300 (1963)]. Dichlorophenylphosphine reacts with COT^{2-} exclusively by 1,2 addition.[2b]

(4) A. G. Anastassiou, *ibid.*, **90**, 1527 (1968); **87**, 5551 (1965).

(5) S. Masamune and N. T. Castellucci, *Angew. Chem., Int. Ed. Engl.*, 3, 582 (1964). The urethane **1c** is unchanged upon heating at 80° for at least 2 hr and further pyrolysis of **3c** affords a complex mixture from which some *N*-carbethoxyindole can be isolated (unpublished observations, this laboratory).

(6) This type of transformation was first observed in the phosphorus case reported by Katz.[2b] A sulfur example was reported recently [A. G. Anastassiou and B. Y-H. Chao, *Chem. Commun.*, 979 (1971)] and two carbon examples have also been reported [A. G. Anastassiou, R. P. Cellura, and E. Ciganek, *Tetrahedron Lett.*, 5267 (1970); D. Schönleber, *Chem. Ber.*, **102**, 1789 (1969)].

(7) D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Commun.*, 146 (1969). We thank Dr. Rees for the experimental details prior to publication.

(8) The nmr spectrum is very similar to that of the corresponding phenylphosphorus derivative (P decoupled).[2b]