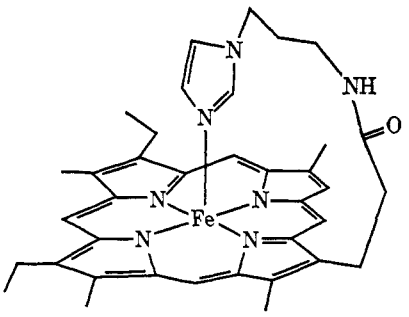

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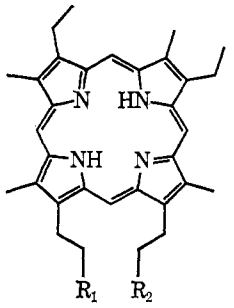
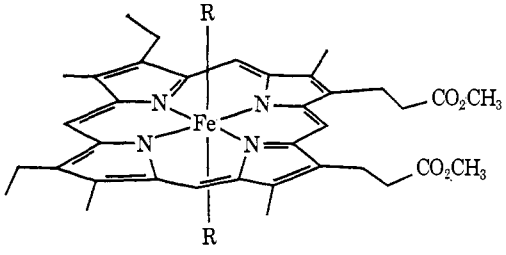


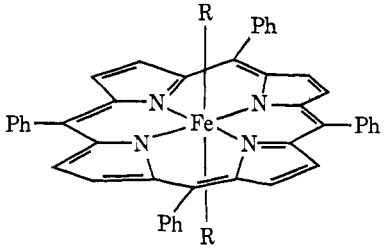
2a, $R_1 = CO_2CH_3$; $R_2 = CONH(CH_2)_3$-imidazole

b, $R_1 = CONH(CH_2)_3$-imidazole; $R_2 = CO_2CH_3$



3a, R = N-methylimidazole

b, R = imidazole



4, R = imidazole

the neighboring group effect of the covalently attached imidazole of **2**, is not necessary for reversible oxygen binding at these low temperatures and low concentrations.

In related experiments we observed that *meso*-tetraphenylporphyrinbis(imidazole)iron(II) (**4**) reacts instantaneously and *irreversibly* with oxygen even at $-78°$ in toluene (10^{-4} *M*). Stoichiometric oxygen determination gave a value of O_2:Fe of 0.21 ± 0.05, which is close to the expected value (0.25) for irreversible autoxidation. The cause of this irreversibility, which is in contrast to other reports,[3] has been traced to the imidazole ligand. Thus unlike the complex **3** with 1-methylimidazole, the related species, mesoporphyrin IX bis(imidazole)iron(II) (**3b**), was irreversibly oxidized in

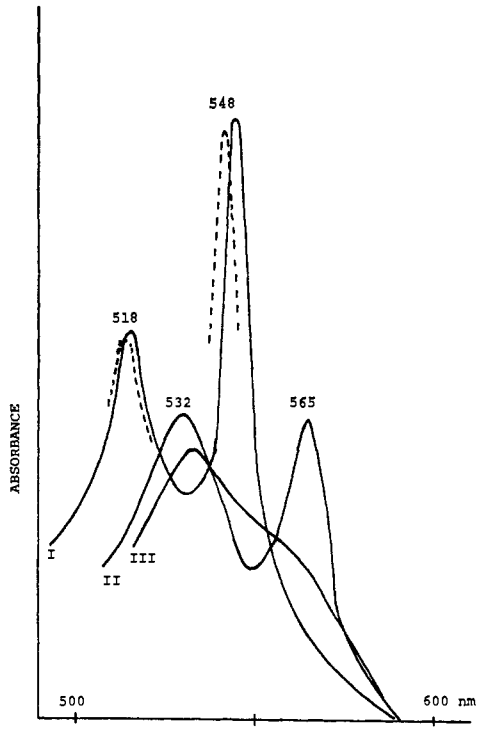


Figure 1. Visible spectra of **2** and **3** in dichloromethane at $-50°$: I, **2** and **3** under argon; II, **2** and **3a** exposed to O_2; III, **3b** exposed to O_2; ----, the hemochrome obtained by addition of pyridine to oxygenated solutions of **2** and **3a**.

dichloromethane (10^{-4} *M*) at $-50°$. Similarly, addition of excess imidazole to the cool ($-50°$) oxygenated solution of the pentacoordinate complex from ligand **2** gave rise to irreversible oxidation, Figure 1.

In summary, dilute solutions of iron(II) complexes of mesoporphyrin IX dimethyl ester reversibly bind oxygen at $-50°$, in the presence of 1-methylimidazole. There is no requirement for a neighboring group effect of a covalently bound ligand to observe this behavior. Also, imidazole causes irreversible oxidation in both the mesoporphyrin IX diester and the *meso*-tetraphenylporphyriniron(II) complexes. The cause of the latter effect is under investigation.

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(12) NSF Predoctoral Fellow, 1971–1974.

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Reaction of Trialkylboranes and 2-Bromo-6-lithiopyridine. Stereospecific Alkylative Cleavage of Pyridine Ring to 5-Alkyl-2(*Z*),4(*E*)-pentadienenitrile

Sir:

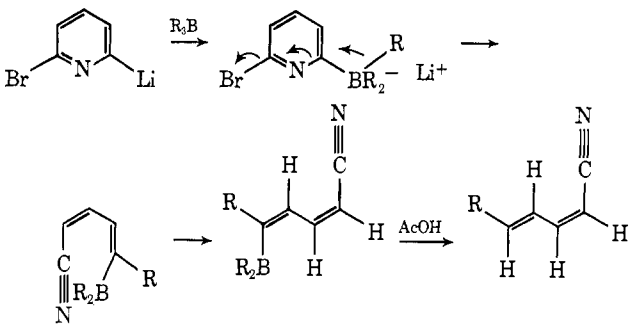
We wish to report the operationally simple, stereospecific procedure affording high yields of 2(*Z*),4(*E*)-

alkadienenitriles from trialkylboranes and 2-bromo-6-lithiopyridine generated from 2,6-dibromopyridine. This procedure is a novel addition to the rapidly growing group of syntheses with organoboranes.[1]

Reaction of tripropylborane and 2-bromo-6-lithiopyridine[2] in ether–hexane solvent afforded 5-dipropylboryl-2(*Z*),4(*E*)-octadienenitrile.[3] Successive treatment with glacial acetic acid gave 2(*Z*),4(*E*)-octadienenitrile in 80% over-all yield. The homogeneity of the dienenitrile was ascertained by glc and also by Eu(fod)$_3$-shifted nmr which established the stereochemistry of the dienenitrile at the same time.[4] Tributylborane afforded 2(*Z*),4(*E*)-nonadienenitrile (93% yield calculated by glc) by the analogous successive treatment with 2-bromo-6-lithiopyridine and with acetic acid. Triisopropylborane, the simplest tri(*sec*-alkyl) borane, gave 6-methyl-2(*Z*),4(*E*)-heptadienenitrile in 60% yield.[5]

The alkylative cleavage of the pyridine ring is explained by assuming the following steps: (1) trialkylborane reacts with 2-bromo-6-lithiopyridine to give lithium (6-bromo-2-pyridyl)trialkylborate;[6] (2) alkyl shift from B to C occurs with inversion of configuration at the olefinic carbon;[7] (3) concertedly with (2) C–N cleavage and elimination of bromide ion proceed.[11]

The following experimental procedure is representative. To a solution of 2-bromo-6-lithiopyridine prepared from 2,6-dibromopyridine (1.18 g, 5 mmol) in 15 ml of anhydrous ether and butyllithium (5.6 mmol in 4 ml of hexane) at −60° through −40° under argon atmosphere,[2] tripropylborane (0.70 g, 5 mmol) was added at −40°. The reaction mixture was stirred at



−40° for 10 min and gradually warmed to room temperature. The resulting mixture was added with 4 ml of glacial acetic acid at room temperature and stirred for 2 hr at room temperature, then 1 hr at reflux. The product was extracted into ether and the ethereal solution was concentrated. Chromatography (silica gel, benzene) of the concentrate gave 2(*Z*),4(*E*)-octadienenitrile (470 mg, 80%): bp 65–75° (5 mm); ir (neat) 2220, 1640, 1580, 990, 950, and 740 cm^{-1}; uv (EtOH) λ_{max} 255 nm; mass spectral *m/e* (rel. intensity %) 121 (M^+, 35), 120 (12), 106 (12), 92 (16), 80 (100), 79 (78); nmr (CCl_4) δ 1.0 (3 H, t, J = 7 Hz), 1.5 (2 H, sextet, J = 7 Hz), 2.3 (2 H, apparent q, J = 7.5 Hz), 5.15 (1 H, d, J = 11 Hz), 6.0–6.9 (3 H, m); Eu(fod)$_3$-shifted nmr (13 mg of 2(*Z*),4(*E*)-octadienenitrile and 55 mg of Eu(fod)$_3$ in 0.35 ml of CCl_4), olefinic protons, δ 7.08 (1 H, d-t, J = 8, 16 Hz), 8.40 (1 H, t, J = 11 Hz), 9.60 (1 H, d, J = 11 Hz), 10.10 (1 H, d-d, J = 11, 16 Hz).[4]

The base-catalyzed opening of pyrimidine ring has been studied mechanistically and synthetically.[14] The above-described alkylative cleavage of the pyridine ring is without precedent and opens a novel procedure for dienenitrile synthesis from easily available 2,6-dibromopyridine and trialkylboranes.

(1) (a) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972; (b) H. C. Brown, *Chem. Brit.*, 7, 458 (1971); (c) G. M. L. Cragg, "Organoboranes in Organic Synthesis," Marcel Dekker, New York, N. Y., 1973.

(2) J. F. Parks, B. E. Wagner, and R. H. Holm, *J. Organometal. Chem.*, **56**, 53 (1973).

(3) The formation of this compound was estimated by the comparison of ir (neat, 2220 cm^{-1}) and uv (EtOH, λ_{max} 268 nm) of the concentrated reaction mixture with those of its protonolysis product, 2(*Z*), 4(*E*)-octadienenitrile.

(4) (a) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971); (b) R. E. Davis, M. R. Willcott, III, R. E. Lenkinski, W. von E. Doering, and L. Birladeanu, *ibid.*, **95**, 6847 (1973), and references cited therein.

(5) 2-Bromopyridine and an unidentified oil were obtained as by-product.

(6) Formation of this borate was reasonably conceived from the analogy to trialkylphenylborate formation from phenyllithium and trialkylborane.

(7) Retention of configuration at the migrating carbon was presumed.[8] Analogous alkyl shift in alkenylborate was reported to proceed with retention of configuration.[9]

(8) According to the suggestion of Professor B. M. Trost, the reaction of 2-bromo-6-lithiopyridine with tris (*trans*-2-methylcyclopentyl)-borane was attempted. The reaction mixture gave only 6% yield of 5-(2-methylcyclopentyl-2(*Z*),4(*E*)-pentadienenitrile whose homogeneity and structure were determined by glc, ir (neat, 2220, 1640, 1580, 990, 950, and 740 cm^{-1}), uv (EtOH, λ_{max} 260 nm), mass spectral (*m/e* (rel intensity %), 161 (M^-, 6), 160 (2), 106 (22), 105 (17), 82 (100), 67 (70)), nmr (CCl_4, δ 0.9–2.5 (11 H), 5.12 (1 H, d, J = 11 Hz), 5.9–6.9 (3 H, m)) and Eu(fod)$_3$-shifted nmr (analogous to the case of 2(*Z*),4(*E*)-octadienenitrile *vide infra*). The stereochemistry of the cyclopentane ring could not be determined by spectrometry but was presumed to be trans.[9] Due to this low yield, stereochemical studies on cyclopentane ring were abandoned. Mixed boranes such as disiamyl-1-octenylborane and 2-hexyl-1,3,2-benzodioxaborole failed to give the desired products. See also ref 10.

(9) G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *J. Amer. Chem. Soc.*, **93**, 6309 (1971).

(10) M. Naruse, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, 1847 (1973).

(11) The concerted $[\sigma 2_s + \sigma 2_s + \sigma 2_s]$ process[12] is symmetry allowed.[13]

(12) When the orbital of boron atom is ignored, this reaction falls into the classification of $[\omega 2_s + \omega 0_a + \omega 2_a + \omega 0_s + \omega 2_s]$.

(13) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Weinheim, 1971.

(14) H. C. Van der Plass and A. Kondijs, *Recl. Trav. Chim. Pays-Bas*, **92**, 711 (1973) and references cited therein.

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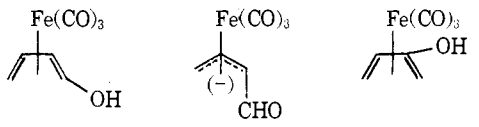
Chemistry of Substituted Hydroxybutadienetricarbonyliron Complexes

Sir:

Although many organic ligands have been complexed to transition metals, few have functional groups attached and in almost no case is the group one, like –OH or –NH_2, which might be useful in probing electronic interactions within the organic portion of the complex. Some time ago[1] we reported the synthesis of *syn*-1-hydroxybutadienetricarbonyliron (I) and of its 2-hydroxy isomer III, enolic compounds which ex-



I II III

(1) C. H. DePuy, R. N. Greene, and T. E. Schroer, *Chem. Commun.*, 1225 (1968).