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Concerning the Superoxide Electrodes in Nitrate Melts

Sir:

This note is written in the hope of preventing confusion that may be caused by an error in a recent communication[1] by Schlegel, concerning oxygen electrode in molten nitrates.

Work in this laboratory has shown[2] that the potential of the superoxide/oxygen electrode in molten (sodium, potassium) nitrate at 503 K can be described by the half-reaction

$$O_2 + e = O_2^- \qquad (1)$$

and that its standard potential, E_1^0 in the equation

$$E = E_1^0 - (RT/F) \ln [O_2^-]/[O_2] \qquad (2)$$

can be deduced both from potentiometric[2] data and from the reversible[2-5] voltammetric half-wave potential of the redox couple O_2/O_2^-: $E_1^0 = E^0_{O_2/O_2^-} = -0.645$ V vs. a Ag/Ag^+ (0.07 *m*) reference electrode.

Schlegel[1] used our data[2] to obtain a different value of the standard potential, $E_2^0 = -1.185$ V, by the unstated assumption that

$$E = E_2^0 - (RT/F) \ln [O_2^-]/p_{O_2} \qquad (3)$$

where p_{O_2} is the partial pressure (atm) of oxygen in equilibrium with the melt. Neither E_1^0 nor E_2^0 is incorrect per se, and both pertain to the redox couple O_2/O_2^-, but they do differ in the choice of the standard state for oxygen, which is a 1 *m* solution (as for superoxide) for E_1^0 and a partial pressure of 1 atm for E_2^0. Because of this difference it is impossible to compare E_2^0 directly with the voltammetric half-wave potential, as Schlegel attempted to do. At the half-wave potential of any couple, ox + *n*e = red, the activities of ox and red are equal if both are contained in the same phase, but *only if they are expressed in the same units.* For the O_2/O_2^- couple the potential at which $p_{O_2} = m_{O_2^-}$ is very different from the half-wave potential.

Schlegel was apparently misled by the fact that the difference between E_1^0 and E_2^0, which involves the Henry's law coefficient[5] for oxygen ($K_H = 4.10^{-6}$ mol kg^{-1} atm^{-1})

$$E_1^0 - E_2^0 = -(RT/F) \ln K_H \qquad (4)$$

is fortuitously almost equal to the difference between the standard[2] (and half-wave[4]) potentials of the O_2/O_2^- and O_2^-/O_2^{2-} couples, which involves the disproportionation constant[2] of superoxide ion

$$2O_2^- = O_2 + O_2^{2-}; K_5 = 5.10^{-7} \qquad (5)$$

so that

$$E^0_{O_2/O_2^-} - E^0_{O_2^-/O_2^{2-}} = -(RT/F) \ln K_5 \qquad (6)$$

Schlegel[1] concluded that the potential of an oxygen electrode under these conditions is governed by the O_2^-/O_2^{2-} couple rather than by the O_2/O_2^- couple. This is not proven by his argument, could not be proven by any purely thermodynamic argument, and has no real meaning at the present time. A potential determining process can be identified only with the aid of kinetic data. At present it is known only that the rate constants for electron transfer at the standard potentials are high enough so that both couples are voltammetrically reversible,[3,6] and they are interrelated through reaction 5, for which both the forward and backward rate constants are also high.[7] Hence it is as yet possible only to identify the half-reaction responsible for the two voltammetric waves and to evaluate their standard potentials, and this was correctly done in our previous studies. The standard potentials (vs. Ag/Ag^+, 0.07 *m*) for the oxygen/superoxide and superoxide/peroxide couples in a (Na, K)NO_3 equimolar melt at 503 K are the following: $E^0_{O_2/O_2^-} = -0.645 \pm 0.005$ V (from both potentiometric[2] and RDE voltammetric[8] data); $E^0_{O_2^-/O_2^{2-}} = -1.26 \pm 0.01$ V (from RDE voltammetric[8] data).

Acknowledgment. Work carried out with the financial assistance of the Italian National Research Council (CNR, Roma).

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$$E^0 = E_{1/2} - (RT/nF) \ln (D_{red}/D_{ox})^{2/3}$$

The diffusion coefficients data for oxygen, superoxide, and peroxide are given in ref 2 and 4.

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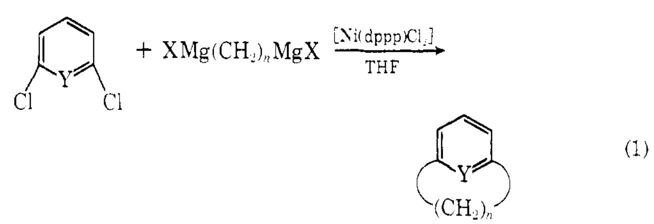
One-Step Preparation of Metacyclophanes and (2,6)Pyridinophanes by Nickel-Catalyzed Grignard Cyclocoupling

Sir:

There is much current interest in the chemistry of cyclophanes and heterophanes;[1] however, the overall product yields in the wide variety of synthetic methods so far developed generally suffer from the multistep sequences involved.[1a,2] We report here a one-step preparation of [*n*]metacyclophanes and [*n*](2,6)pyridinophanes by the cyclocoupling of di-Grignard reagents with aromatic dihalides in the presence of catalytic quantities of a nickel-phosphine complex



(1)

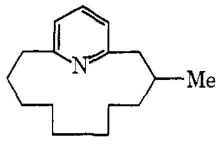
1, Y = N; a, n = 6 11%
b, n = 7 10%
c, n = 8 16%
d, n = 9 15%
e, n = 10 33%
f, n = 12 26%
2, Y = CH; a, n = 8 3%
b, n = 9 9%
c, n = 10 22%
d, n = 12 18%

and utilization of the method to synthesize muscopyridine.

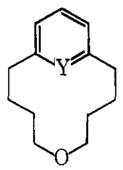
The cyclocoupling is effected merely by adding a THF solution of a di-Grignard reagent under nitrogen to a well-stirred mixture of an equimolar quantity of a dihalide in THF containing a catalytic amount of dichloro[1,3-bis(diphenylphosphino)propane]nickel(II), [Ni(dppp)Cl$_2$]. The reaction mixture is stirred at room temperature or at 40° for up to 20 hr. The Grignard cyclocoupling is based on the recently reported selective cross-coupling of Grignard reagents with aryl halides catalyzed by phosphine-nickel complexes,[3] and an appropriate choice of reaction conditions may be required for the cyclization. The following method, if not necessarily optimum, gives the best yields: (1) slow dropwise addition of the Grignard reagent, (2) maintenance of reaction temperatures within the range 30-40°, and (3) limited concentration of nickel catalyst, i.e., mole ratio catalyst/dihalide = 0.05 for dichlorobenzene and 0.005-0.01 for dichloropyridine. Some representative homologous series (eq 1) have been prepared in fair to good yields[4] which may be compared with the low yields in the traditional multistep syntheses.[5,6] The higher yields of pyridinophanes as compared to metacyclophanes are noteworthy and may be attributable primarily to the smaller steric size of =N- than =CH-.[1e,7]

The synthetic advantage of the novel cyclophane synthesis is exemplified by the first successful preparation of [6](2,6)pyridinophane (**1a**) which contains the shortest methylene bridge ever reported for the (2,6)pyridinophane system:[8] NMR δ (100 MHz, CCl$_4$, 31.5°) 1.3-1.6 (narrow m, 4 H), 1.6-1.9 (m, 4 H), 2.83 (t, J = 3.0 Hz, 4 H), 6.76 (d, J = 3.8 Hz, 2 H), 7.34 (t, J = 3.8 Hz, 1 H); uv (ethanol) λ_{max} (log ϵ) 211.5 (3.85), 271.5 nm (3.50); m/e 161 (M$^+$). The main feature of the NMR spectrum of **1a** is the absence of a strong shielding effect of the π electron cloud on the polymethylene chain. This result is different from the situation found in [6]metacyclophane and analogs[8] and [7](2,6)pyridinophane (**1b**).[5c] A sharp triplet due to the C$_1$ and C$_6$ methylene protons is indicative of rapid flipping of the hexamethylene chain to either side of the pyridine ring, whereas the aliphatic chain of [6]metacyclophanes is conformationally locked on one side of the aromatic ring.[8] At low temperature (−92.5°, CCl$_3$F, 60 MHz) two of four methylene protons on C$_3$ and C$_4$ appear at δ 0.71 as a multiplet. The coalescence temperature is ca. −40° and the energy barrier to flipping was estimated to be 11.0 kcal/mol which is much higher than the 9.0 kcal/mol for **1b**.[5c] The uv spectrum of **1a** is essentially the same as that of **1b** and suggests comparable distortion of the pyridine ring.

The application of the cyclocoupling is further exemplified by the preparation of racemic muscopyridine (**3**), the *d* form of which is one of the odoriferous constituents of natural musk from the musk deer (*Moschus moschiferus*).[9] Thus **3**, previously prepared in very low yield in multisteps from cyclododecanone,[5a] was obtained in 20% yield by the reaction of the di-Grignard reagent of racemic 2-methyl-1,10-dibromodecane[10] with 2,6-dichloropyridine in the presence of [Ni(dppp)Cl$_2$].[4,11]



3



4, Y = N
5, Y = CH

The novel cyclophane synthesis is not solely restricted to the homomethylene bridges, and oxamethylene bridged compounds, **4** and **5**,[4] were similarly prepared in ca. 20% yield from the appropriate di-Grignard reagent which suggests a possible new route to macrocyclic polyethers.

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(11) This may be the second example of the total synthesis of natural products using a nickel-catalyzed C–C bond formation; cf. W. E. Billups, J. H. Cross, and C. V. Smith, *J. Am. Chem. Soc.*, **95**, 3438 (1973).

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