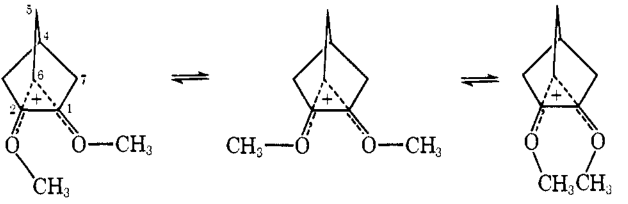
tached to cationic centers and reveal that C-2 is essentially trigonally hybridized.[4,5,6] The small separation (0.06 ppm) in the two methoxyl peaks in **1**$^+$ indicates existence of *syn* and *anti* forms due to restricted rotation about the C–O bond or to restricted oxygen inversion. This interpretation is confirmed by the existence of two signals for the C-1 proton in the same ratio, 1:4. The *anti* structure appears less congested and is assigned to the predominant form. Cation **2**$^+$ shows only one methoxyl peak, which is very likely the *anti* form because of hindrance by the CH_3 group at C-1.[9]

In the conversion of **2** → **2**$^+$ the large shift ($\Delta\delta = 1.53$) in the C-2 methoxyl and the small shift ($\Delta\delta = 0.15$) in the C-1 methyl resonances are in accord with the classical formulation for **2**$^+$ in which C-2 is essentially sp^2 while C-1 is sp^3 hybridized.

The nmr of the 1,2-dimethoxy-2-norbornyl cation (**3**$^+$) showed temperature dependence. The spectrum at −68° (Table I) persisted until *ca.* −15° at which stage line broadening began and at 7°, among other changes, the two methoxyl signals coalesced. Importantly, the original spectrum was regenerated when the temperature was lowered to −60°. At coalescence (7°) the first-order rate constant[4] for exchange of the OCH_3 magnetic environment is 251 sec^{-1}, and $\Delta G^{\ddagger} = 13.2$ kcal/mol. Table II shows that at 38.5° the spectrum of cation **3**$^+$ is completely averaged. The signals fall into five distinct groups whose assignments are supported by the decoupling results. As expected, the single methoxyl peak (δ 4.35) is at the mean position (δ 4.33) of the two methoxyl signals in the low-temperature spectrum.

That **3**$^+$ does not possess a carbon-bridged structure **4** which could exist in three distinct geometric forms (**4a–c**) is clear from the following considerations, among others. (i) Substrates **1** and **2** (Table I) as well as others in the literature[6b] reveal that a methoxyl signal moves downfield ($\Delta\delta$) by *ca.* 1.5–1.6 ppm when a ketal is converted to a tertiary cation by OCH_3 loss.[10] For **3** → **3**$^+$ $\Delta\delta$ is 1.70 for the C-2 methoxyl and 0.41 for the C-1 methoxyl. Clearly, the cation has one oxygen attached to a trigonal cationic center while the other remains bound to an sp^3 carbon which is only slightly perturbed electronically. (ii) The large separation (1.13 ppm) between the two methoxyl peaks in **3**$^+$ (Table I) is not understandable in terms of *syn,anti* differences (**4a–c**).[11] (iii) Symmetry requires that for the nonclassical structure to show two *equal intensity* methoxyl peaks, **4b** and **4c** would have to contribute equally or not at all to the low-temperature conformational population, a situation that is hardly likely.



syn, anti **4a** *anti, anti* **4b** *syn, syn* **4c**

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[9] Alternatively, a very low *syn,anti* barrier could produce a single "averaged" methoxyl peak but this possibility is ruled out by the results with **1**$^+$ and by published data on barriers of this sort.[6b]

[10] We have also examined camphor dimethyl ketal and found $\Delta\delta = 1.58$.

[11] Compare **1**$^+$. Also in other known *syn,anti* situations (*e.g.*, $R{-}C^+{-}(OCH_3)_2$; R = CH_3 or OH) the two methoxyls are less than 0.3 ppm from each other.[4,6b]

Do Aromatic Pinacols Oxidize at a Mercury Electrode?

Sir:

Michielli and Elving[1] recently put in doubt the reality of the anodic oxidation of benzpinacol previously described by us.[2,3] They report under the heading "Reputed Benzpinacol Oxidation"[1] an unsuccessful attempt to reproduce the anodic polarographic wave of benzpinacol in alkaline aqueous ethanol solutions.

Nevertheless, our conclusion on the anodic oxidation of benzpinacol is well founded experimentally. We have examined not only benzpinacol but also fluorenopinacol, xanthopinacol, and 4-chlorobenzpinacol, which behave quite analogously.[4–6] Anodic oxidation in alkaline or neutral solutions seems to be a general property of aromatic pinacols.

We have prepared the pinacols by several methods: controlled-potential electrolysis, photoreduction, or chemical reduction of ketones. The compounds were thoroughly purified and checked as to their identity and purity before use.

The anodic oxidation follows quantitatively the kinetics of a slow electron-transfer reaction with pinacol monoanion as a depolarizer. Oxidation proceeds with a C–C bond rupture, to ketone as a product. The electron-transfer step is preceded by a protolytic dissociation of a pinacol to its monoanion. The rate of this proton-transfer step determines the oxidation current near pH 7.

The oxidation wave is proportional to the pinacol concentration. This wave was quantitatively interpreted in terms of the kinetics and thermodynamics of dimerization of ketyl free radicals,[5,6] and the values obtained were confirmed independently. In the course of dimerization, or at varying pH of the solution, the pinacol oxidation wave appears at the cost of the anodic wave of ketyl free radicals.

In alkaline solutions pinacols undergo dismutation, *e.g.*, eq 1. In the course of reaction 1 the anodic

$$\mathrm{Ph_2COH{-}COHPh_2 \longrightarrow Ph_2C{=}O + Ph_2CHOH} \qquad (1)$$

pinacol wave slowly disappears (its kinetics were quantitatively studied),[6] while the current of the first cathodic wave of ketone increases about 1:2 with respect to the decrease of the anodic wave (see Figure 1).

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[1] R. F. Michielli and P. J. Elving, *J. Am. Chem. Soc.*, **90**, 1989 (1968).

[2] W. Kemula, Z. R. Grabowski, and M. K. Kalinowski, *Collection Czech. Chem. Commun.*, **25**, 3306 (1960).

[3] W. Kemula, Z. R. Grabowski, and M. K. Kalinowski, *Naturwissenschaften*, **47**, 514 (1960).

[4] Z. R. Grabowski and M. K. Kalinowski, The Fifth International Symposium on Free Radicals, Almqvist & Wicksell, Publishers, Stockholm, 1961, paper 22.

[5] M. K. Kalinowski, Z. R. Grabowski, and B. Pakula, *Trans. Faraday Soc.*, **62**, 918 (1966).

[6] M. K. Kalinowski and Z. R. Grabowski, *ibid.*, **62**, 926 (1966).

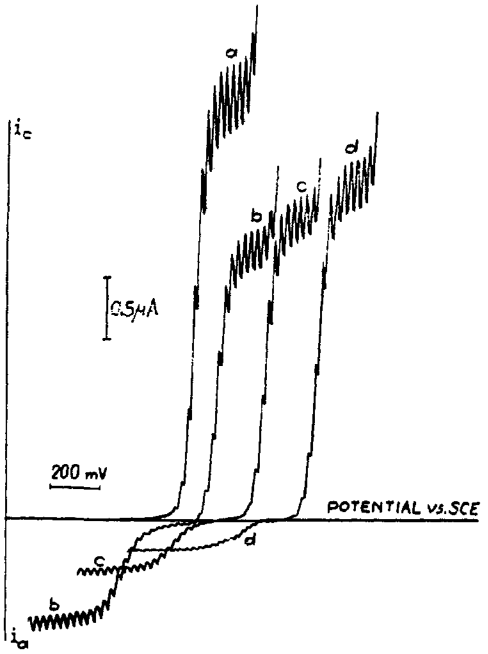

Figure 1. Polarographic curves of 1.3×10^{-3} *M* fluorenone in aqueous 38 vol % ethanol, 0.15 *M* NaOH, at 24°: (a) before electroreduction; (b) just after stopping a controlled-potential ($E = -1100 \pm 10$ mV *vs.* sce) electrolysis of 10-min duration; (c) 15 min later; (d) 30 min later. All curves begin at −0.3V.

It is difficult to explain why Michielli and Elving could not observe the anodic wave of benzpinacol.[1] Most probably, benzpinacol was absent in their sample at the moment of recording a polarogram. Perhaps their "commercial benzpinacol, used as received,"[1] did not already contain the compound, or the pinacol decomposed in solution prior to the measurement. Benzpinacol is easily oxidized to benzophenone, undergoes dismutation (1) in the presence of traces of base, and isomerizes to benzopinacoline. It must be thoroughly checked before use and the solutions must be prepared with necessary precautions.

Our conclusions are further supported by recent results of Nekrasov and Korsun[7,8] who studied the reduction of aromatic ketones on a rotating disk–ring electrode and found the anodic waves of benzpinacol and fluorenopinacol oxidation. All available evidence, with the exception of the report of Michielli and Elving, confirms that aromatic pinacols oxidize at a mercury anode.

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[8] A. D. Korsun and L. N. Nekrasov, *Elektrokhimya*, **4**, 1501 (1968).

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Oxidation of Benzpinacol in Alkaline Solution

Sir:

In a study of the electrochemical reduction of benzophenone in pyridine,[1] the statement was made that the oxidation of benzpinacol to benzophenone at the dme in alkaline aqueous ethanol solution (0.12 *M* NaOH in 68% (v/v) EtOH), as reported by Kemula, *et al.*,[2] could not be duplicated; this was ascribed to chemical decomposition of the pinacol before it could be measured. This work has been repeated under conditions which minimize decomposition of the pinacol and the oxidation previously reported[2] has been observed.

Three samples of benzpinacol—prepared chemically, electrochemically, and photochemically—were examined in the solution composition indicated by direct current polarography (scan rate of 0.2 V/min) and an anodic wave was observed with $E_{1/2}$ of −0.60 V (−0.58 V previously reported[2]), which decreases with time while the benzophenone cathodic wave increases. The rate of decrease in height of the anodic wave increases markedly as the alkalinity increases.

Acknowledgment. The authors thank James E. O'Reilly and Conrad O. Schmakel, who performed the experiments indicated.

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On Energy Localization of Approximate Molecular Orbitals[1]

Sir:

Energy-localized molecular orbitals (LMO's) obtained from the Edmiston–Ruedenberg (ER) method[2] are useful since they conform to intuitive ideas of chemical bonding. Applications of this method using semiempirical molecular orbitals are of particular interest since such MO's are at present readily available for a much wider range of molecules than are *ab initio* orbitals. Trindle and Sinanoğlu[3a] have recently applied the ER localization method to the CNDO/2[3b] molecular orbitals of several molecules; however, some of their results, especially for unsaturated systems, do not agree with the corresponding LMO's obtained from *ab initio* calculations.[4-6] In addition, it has been shown[7] that the fact that CNDO spherically averages electron-repulsion integrals can lead to an indeterminacy in the resulting LMO's. It is the purpose of this note to demonstrate that the less approximate INDO theory[8] is a more appropriate method to use for localization. Since INDO includes distinguishable one-center integrals, one would expect this method to give a more reasonable description of the atomic components of a molecule and thus of the canonical and localized orbitals as well.

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2583.

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