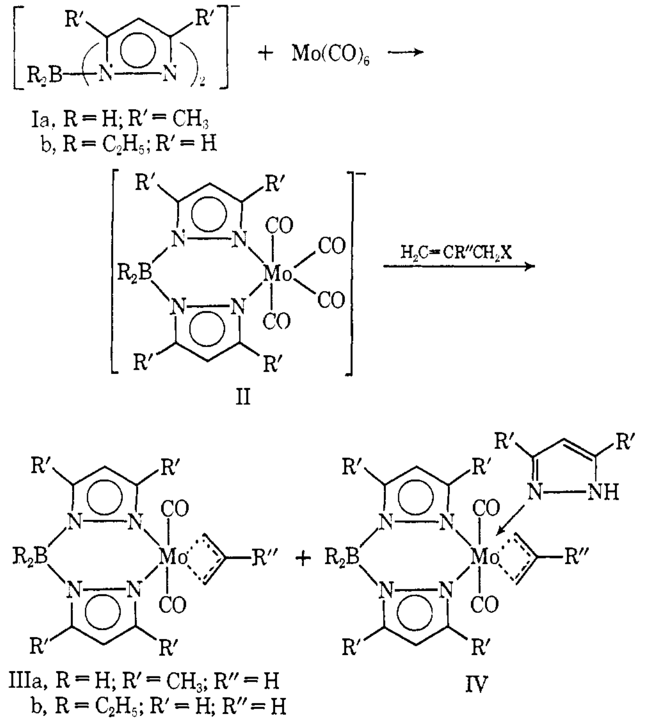
Molybdenum Complexes with Non-Inert-Gas Configuration

Sir:

A wide variety of organometallic compounds has been produced by the reaction with suitable electrophiles of carbonyl anions $LM(CO)_3^n$ (where L = tridentate, or formally tridentate, ligand; $n = -1, -2$; M = group VIB metal, particularly molybdenum), obtained by the reaction between L^n and $M(CO)_6$. The main types of ligand L are the cyclopentadienide[1] and the trispyrazolylborate[2] ions as well as the various carbollide ions,[3] *e.g.*, (3)-1,2-$B_9C_2H_{11}^{2-}$. By contrast, the analogous area based on anions derived from uninegative bidentate ligands and group VIB carbonyls is unknown.[4] We have found that such compounds are readily accessible by the reaction of appropriately substituted dipyrazolylborate ions with molybdenum hexacarbonyl. Of particular interest are derivatives of structure III which possess a noninert gas configuration (16 electrons).



Ia, $R = H; R' = CH_3$
b, $R = C_2H_5; R' = H$

II

IIIa, $R = H; R' = CH_3; R'' = H$
b, $R = C_2H_5; R' = H; R'' = H$

IV

Heating of Ia with molybdenum hexacarbonyl in dimethylformamide yields the anion II, isolable as the tetraethylammonium salt, which is much less stable than the analogous $RB(pz)_3Mo(CO)_3^-$ salt. However, it reacts smoothly with allyl bromide forming in 60% yield an orange-red, sublimable solid, mp 165–166°, of excellent stability to air and moisture which was assigned structure IIIa from the following data. *Anal.* Calcd for $C_{15}H_{21}BMoN_4O_2$: C, 45.4; H, 5.31; N, 14.1; mol wt, 396. Found: C, 45.6; H, 5.31; N, 14.1; mol wt (osmometric in chloroform), 396. The infrared spectrum (in cyclohexane) had a sharp boron–hydrogen stretch singlet at 2483 cm^{-1} and two strong carbonyl bands at 1964 and 1874 cm^{-1}. The B^{11} nmr spectrum consisted of a triplet (J = 90 cps) at +33.2 ppm upfield from trimethyl borate, confirming the presence of a BH_2 group. Finally, the limiting[5] high-temperature nmr spectrum at 60° showed the presence of a normal π-allyl (doublets at τ 6.49 (J = 7.5 cps) and 8.60 (J = 10.5 cps) and multiplet at 5.96 in 2:2:1 ratio) and the dihydrobis(3,5-dimethyl-1-pyrazolyl)borate ligand (singlets at τ 4.33, 7.50, and 7.93 in 2:6:6 ratio assigned to the 4-H, 3-CH_3, and 5-CH_3, respectively).

When the same reaction sequence was carried out using Ib, two products were isolated. The first was an orange solid, mp 127–129° dec, which was again assigned the analogous structure IIIb on the basis of analysis (*Anal.* Calcd for $C_{15}H_{21}BMoN_4O_2$: C, 45.4; H, 5.31; N, 14.1. Found: C, 45.6; H, 5.38; N, 14.3), the infrared spectrum, which contained two strong carbonyl bands at 1964 and 1878 cm^{-1}, and the nmr spectrum which showed the presence of one diethylbis(1-pyrazolyl)borate ligand and one normal π-allyl group: doublets at τ 1.85 (J = 2.1, J' = 0.5 cps) and 2.57 (J = 2.3, J' = 0.5), triplet at 3.78 (J = 2.2), doublet (J = 7.0) at 6.30 overlapped by a complex multiplet (τ 5.8–6.3), doublet (J = 9.5) at 8.41, a broad peak at 9.16, and a multiplet at 12.4 in 2:2:2:3 (doublet + multiplet):2:8:2 ratio. These were assigned to the 3-H, 5-H, 4-H, the 1-allyl H overlapping the allylic 2-H, the allylic 3-H, the overlapping pseudoequatorial B-ethyl plus the other CH_3 group, and, finally, the pseudoaxial methylene. The shift of the pseudoaxial methylene is comparable in magnitude but different in direction from that observed in $Ni[Et_2B(pz)_2]_2$.[6] The fact that resonance of the pseudoaxial methylene occurs as high as τ 12.4 implies a certain degree of "hydridic" character, and molecular models suggest that the two hydrogens are intruding into a suitable empty metal orbital. Support for this hypothesis may be found in the presence of CH stretch bands at remarkably low frequency (2704, 2664 cm^{-1}) implying again some sort of hydrogen bridging between the pseudoaxial methylene and the transition metal.

Upon coordination of pyrazole (*vide infra*) or of any other base, the unique methylene disappears and both boron-bonded ethyl groups become normal (*i.e.*, resembling those in 4,4,8,8-tetraethylpyrazabole,[7] diethylborylimidazoles,[8] or N,N'-bis(diethylboryl)oxamidines[9]). Furthermore, the low-frequency CH stretch band disappears in the infrared spectrum.

The other product was a yellow solid, mp 131–132°, assigned structure IV. *Anal.* Calcd for $C_{18}H_{24}BMoN_6O_2$: C, 46.5; H, 5.39; N, 18.1. Found: C,

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(1) *Cf.* R. B. King, *Advan. Organometal. Chem.*, **2**, 190 (1964).

(2) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 4904 (1967).

(3) M. F. Hawthorne, D. C. Young, J. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. Wegner, *ibid.*, **90**, 879 (1968).

(4) In fact, only a few systems containing a β-diketonate moiety bonded to a metal carbonyl have been reported: F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964); F. A. Hartman, M. Kilner, and A. Wojcicki, *Inorg. Chem.*, **6**, 34 (1967); F. Bonati and R. Ugo, *J. Organometal. Chem.*, **11**, 341 (1968).

(5) The nmr spectrum of this compound was temperature dependent. The limiting low-temperature (−20°) spectrum showed each of the π-allyl hydrogens to be in a different environment and also indicated nonequivalence of the two 4-H's and the 3-CH_3 groups. The temperature dependence of the nmr spectrum of this and of other compounds of related structure (to be published) is consistent with rotation or pseudorotation of the π-allyl group, similar to that found in $C_5H_5Mo(CO)_2$-π-CH_2CRCH_2 systems: A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967); J. W. Faller and M. J. Incorvia, *ibid.*, **7**, 840 (1968).

(6) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 6288 (1967).

(7) S. Trofimenko, *ibid.*, **89**, 3165 (1967).

(8) S. Trofimenko, *ibid.*, **89**, 3903 (1967).

(9) S. Trofimenko, *ibid.*, **89**, 7014 (1967).

46.2; H, 5.50; N, 18.0. The infrared spectrum showed, apart from carbonyl peaks at 1942 and 1857 cm^{-1}, the NH band at 3398 cm^{-1}. The nmr spectrum clearly demonstrated presence of the $Et_2B(pz)_2$ ligand and of one additional pyrazole: s (broad) τ 1.30, d (unresolved) 2.02, d (J = 2.0 cps) 2.21, d (J = 2.4) 2.31, d (unresolved) 2.94, t (J = 2.2) 3.83, m 5.8, d (J = 7.0) 6.62, d (J = 9.5) 8.43, m ~9.1, and "d" at 9.66 in a 1:1:2:2:1:3:1:2:2:5:5 ratio. These were assigned to the NH, 3-H of pyrazole, 3-H's of ligand, 5-H's of ligand, 5-H of pyrazole, 4-H's of pyrazole and ligand, allylic 1-H, allylic 2-H, allylic 3-H, pseudoaxial ethyl, and pseudoequatorial ethyl, respectively. Compound IV could be obtained directly by treatment of IIIb with pyrazole.

Compound IIIb formed yellow complexes possessing inert-gas electronic configuration with other nucleophiles as well, as could be anticipated from its coordinate unsaturation. Failure of IIIa to form comparable complexes may be rationalized on steric grounds. A variety of other stereochemically nonrigid and coordinately unsaturated, yet surprisingly stable, compounds of the general structure III (*e.g.*, R = H, R′ = R″ = CH_3, mp 179–180°; R = H, R′ = CH_3, R″ = C_6H_5, mp 156–157°; R = H, R′ = C_2H_5, R″ = H, mp 104–105°; R = H, R′ = C_2H_5, R″ = C_6H_5, mp 91–92°) has been synthesized and identified similarly. Details of this work and the chemistry of such compounds will be the subject of subsequent publications.

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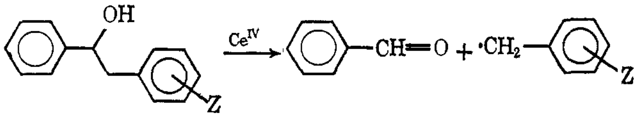
Oxidation of Organic Compounds with Cerium(IV). V. The Substituent Effect on the Rate of the One-Electron Oxidative Cleavage of 2-Aryl-1-phenylethanols[1]

Sir:

We have found that cerium(IV) quantitatively cleaves 1,2-diarylethanols to a benzaldehyde and products derived from the cleaved benzyl moiety. In this communication, we report results that show that this cleavage is a one-electron oxidation and establish the effect of substituted 2-phenyls on the rate of the cleavage reaction. We believe that this reaction is an excellent prototype for one-electron oxidation cleavages of alcohols.



The products of the oxidation of 1,2-diphenylethanol (0.08 *M*) in 75% aqueous acetonitrile by 4 equiv of ceric ammonium nitrate at 90° for 5 min have been found to be 60% benzaldehyde, 30% benzyl alcohol, and 10% benzyl nitrate by nmr and glpc analysis. Oxidation in the presence of 10% acrylamide leads to exclusive formation of benzaldehyde and a polymer with no benzyl alcohol or nitrate. Since acrylamide has been shown to be an effective radical trap,[2,3] these experiments clearly establish that the benzyl alcohol and nitrate arise from a cleaved benzyl radical.

The most reasonable mechanism for the cerium(IV) oxidation of 1,2-diarylethanols is that proposed for the cerium(IV) oxidation of other alcohols, namely the rapid formation of a 1:1 complex followed by slow decomposition of this complex.[4] The fact that the orange cerium(IV) solution turns red when mixed with a 1,2-diarylethanol supports the formation of a 1:1 complex.

$$\mathrm{Ce^{IV}} + \mathrm{ROH} \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow[\text{rate determining}]{k} \text{products} \qquad (1)$$

Competition experiments were carried out by oxidizing two 2-aryl-1-phenylethanols with ceric ammonium nitrate in 75% aqueous acetonitrile. The initial concentration of each alcohol was 0.08 *M* and that of the ceric ammonium nitrate was 0.16 *M*. After the oxidation, the amounts of unreacted alcohols were measured by glpc analysis.[5] With the assumptions that the mechanism of the cerium(IV) oxidation of 1,2-diarylethanols is that given by eq 1 and the equilibrium constants for complex formation are the same for all 1,2-diarylethanols, the relative rates of the decomposition of the complexes are given by eq 2[6] where X_0 and X_f are

$$k_X/k_Y = \frac{\log (X_0/X_f)}{\log (Y_0/Y_f)} \qquad (2)$$

the initial and final concentrations of alcohol X and Y_0 and Y_f are the initial and final concentrations of alcohol Y. The assumption that the equilibrium constants for complex formation are the same for all 1,2-diarylethanols is quite reasonable since we have found[7] that the equilibrium constants for complex formation between cerium(IV) and substituted benzyl alcohols are not very sensitive to electronic effects.

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[1] (a) Part IV: W. S. Trahanovsky, L. B. Young, and G. L. Brown, *J. Org. Chem.*, **32**, 3865 (1967); (b) this work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences; (c) based on work by P. M. N. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

(2) G. Mino, S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959). These workers quantitatively analyzed for acetone by an involved spectrophotometric method and carried out no control experiments to ascertain whether or not the high concentration of an amide affected the reaction. We essentially repeated their study[3] using bicyclohexyl-1,1′-diol which produced cyclohexanone which could be accurately analyzed directly by glpc methods that are now available and also carried out the oxidation in the presence of 10% acetamide. Our results agreed with their results, and the acetamide had no significant effect on the reaction.

(3) Unpublished work of W. S. Trahanovsky, L. H. Young, and M. H. Bierman.

(4) (a) W. H. Richardson in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 247–255, and references therein; (b) K. V. Rao and S. S. Muhammad, *Bull. Chem. Soc. Japan*, **36**, 943 (1963); (c) S. S. Muhammad and K. V. Rao, *ibid.*, **36**, 949 (1963); (d) M. Rangaswamy and M. Santappa, *Current Sci.* (India), **34**, 282 (1965); (e) B. Sethuram and S. S. Muhammed, *Acta Chim. Acad. Sci. Hung.*, **46**, 115, 125 (1965); (f) B. Sethuram, *Current Sci.* (India), **35**, 254 (1966); (g) M. Rangaswamy and M. Santappa, *ibid.*, **35**, 332 (1966); (h) H. L. Hintz and D. C. Johnson, *J. Org. Chem.*, **32**, 556 (1967).

(5) Benzophenone was used as an internal standard. Relative extraction and thermal conductivity ratios were corrected for by extracting and analyzing known amounts of 2-aryl-1-phenylethanols and standard from an artificial reaction mixture that had been prepared by the reduction of ceric ammonium nitrate in 75% aqueous acetonitrile by pinacol hydrate. All analyses were based on at least three independent runs.

(6) G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

(7) Unpublished work of L. B. Young and W. S. Trahanovsky.