An analytical sample was obtained by preparative glpc (2-ft SE 30, programmed at 10°/min, start 100°, Chromosorb 45–60 W).

Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.7; H, 10.1.

23 *via* **Hydrogenation of 24.** Olefin **24**, 166 mg, was hydrogenated in 4 ml of acetic acid with 30 ml of 5% palladium on charcoal at 2 atm, 20°, for 16 hr. Removal of the catalyst by filtration through Celite and evaporation of the solvent at reduced pressure yielded an oil which was chromatographed on 20 g of alumina (Woelm, activity grade I). Elution with 16% benzene in hexane yielded 156 mg of **23**. A mixture of this and the Wolff–Kishner product **23** from aldehyde **22** had identical retention times on two columns: 6-ft Carbowax 20M, 250°, 60–80 S and 8-ft Apiezon L, 270°, 60–80 S. The nmr spectrum had minor peaks presumably due to product from *trans* hydrogenation: ir 1380, 1360 cm^{-1}; nmr δ 0.82 (resolved half of doublet), 0.95 (*gem*-dimethyl group and low-field half of doublet), 3.74 (s, 3), 0.78, 0.87, 1.02 (extraneous peaks).

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.9; H, 10.8.

Hydrogenation of 24 with Platinum Oxide. A sample of **24** was hydrogenated in the same manner as the Wolff–Kishner product. A similar ratio (3:2) of the methoxylated and demethoxylated compounds was observed. A mixture of the products obtained from the two different routes had the same glpc retention times as each injected separately (8-ft Apiezon L, 270°, 60–80 S).

Communications to the Editor

Arene–Metal Complexes. I. Thermodynamic Stabilities of Substituted Benzyl Cations Complexed with Tricarbonylchromium[1]

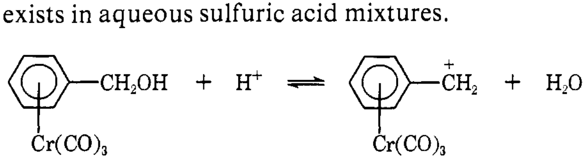
Sir:

The rapid rate of solvolysis of (benzyl chloride)tricarbonylchromium compared to the uncomplexed benzyl chloride has led Holmes, Jones, and Pettit to postulate that the complexed benzyl cation is extraordinarily stable.[2] It is reported, however, that the complexed cation cannot be isolated since rapid decomposition occurs when (benzyl alcohol)tricarbonylchromium is treated with strong acids.[2] We have found that the electronic spectrum of the complexed cation can be measured in sulfuric acid if two precautions are taken. First, the sulfuric acid must be thoroughly purged with nitrogen before use since the complexed cation is sensitive to oxygen. Second, only dilute solutions of the cation must be generated since the cation decomposes by a higher than first order process. In this communication we report the results of a study of the pK_{R^+} values of substituted benzyl cations complexed with tricarbonylchromium. These pK_{R^+} values were measured in aqueous sulfuric acid by Deno's method.[3]

Upon adding an ethanol or acetic acid solution of the substituted (benzyl alcohol)tricarbonylchromiums[4] to moderately (>80%) concentrated sulfuric acid solutions, new absorption bands appear in the ultraviolet–visible spectrum. For example, the spectrum of (benzyl alcohol)tricarbonylchromium in 95% ethanol is 217 (25,800),[7] 254 (6410), and 316 (9650). In 41.0% H_2SO_4, this spectrum is 216 (26,600), 253 (6020), and 313 (9800). In 85–87% H_2SO_4, however, the spectrum that complexed benzyl alcohol gives rise to is 201 (27,800), 278 (11,500), 348 (1500), and 514 (365).

Two experiments were performed which indicate that the formation of the species responsible for the spectrum in the concentrated sulfuric acid can be reversed. A solution of the complex in 82.6% sulfuric acid (violet) was poured onto ice to give a 52.5% sulfuric acid solution (yellow). The λ_{max} values and absorbances of the electronic spectrum of this yellow solution agreed within 2 mμ and about 10% in absorbance to the electronic spectrum of the (benzyl alcohol)tricarbonylchromium in 41.0% sulfuric acid. Another solution of the complex in 85% sulfuric acid was poured onto ice and an ether extraction and conventional work-up gave a 58% isolated recovery of the starting material (verified by nmr, ir, melting point, and mixture melting point). The 58% recovery is a high recovery since using the same procedure only 63% of (*p*-methylbenzyl alcohol)tricarbonylchromium was recovered from 51% sulfuric acid in which it is in the alcohol form.

Since the spectrum of (benzene)tricarbonylchromium is essentially the same in 95% ethanol and 41–97% sulfuric acid mixtures, the spectral changes for the complexed benzyl alcohols cannot be a result of protonation of the aromatic ring or the tricarbonylchromium moiety. Thus we believe that the spectrum of (benzyl alcohol)tricarbonylchromium in concentrated sulfuric acid is that of the benzyl cation complexed with tricarbonylchromium and that the equilibrium shown in eq 1 exists in aqueous sulfuric acid mixtures.



(1)

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(1) (a) This work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences; (b) based on work by D. K. W. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

(2) J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, **4**, 324 (1965).

(3) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3044 (1955).

(4) The (benzyl alcohol)tricarbonylchromium complexes were prepared from (triacetonitrile)tricarbonylchromium and benzyl alcohol following the procedure of King.[5] The complexes were purified by chromatography on silica gel, sublimation, and/or recrystallization (melting points: parent, 92.5–94° (lit.[6] 95.5–96.5°); *p*-methoxy, 60–62°; *p*-methyl, 80–82°; *p*-chloro, 88–89°, 2,4,6-trimethyl, 101–103°). The nmr spectra of the complexes were consistent with their structures and all had signals at δ 5.3 which are characteristic of protons on benzene rings complexed with tricarbonylchromium. Acceptable elemental analyses were obtained for the new tricarbonylchromium complexes.

(5) R. B. King, *J. Organometal. Chem.*, **8**, 139 (1967).

(6) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(7) The wavelength is in mμ and the molar extinction coefficient is given in parentheses.

Table I. Values of pK_{R^+} for Various Carbonium Ions and Rates of Solvolysis of the Corresponding Aralkyl Chlorides in Aqueous Acetone

Carbonium ion	pK_{R^+}	k_{rel}
Ph_3C^+	-6.6^a	2.2×10^9 ^{b}
π-[2,4,6-$(CH_3)_3C_6H_2CH_2$]-[$Cr(CO)_3$]$^+$	-9.3^c	
π-[$PhCH_2$][$Cr(CO)_3$]$^+$	-11.8^c	2.2×10^5 ^{d}
Ph_2CH^+	$-13.3,^a$ -13.4^c	6.9×10^4 ^{d}
2,4,6-$(CH_3)_3C_6H_2CH_2^+$	$-17.3,^e$ -17.0^c	
$PhCH_2^+$	$<-17.3^e$	$(1.00)^d$

[a] Reference 3. [b] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962. [c] This study. [d] Reference 2. [e] N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *J. Am. Chem. Soc.*, **82**, 4719 (1960).

In Table I values of pK_{R^+} ($-\log K$ for the reverse of eq 1) for various carbonium ions and rates of solvolysis of the corresponding aralkyl chlorides are presented. From the pK_{R^+} values one sees that the benzyl cation complexed with tricarbonylchromium is about as stable as the benzhydryl cation and greater than 5.5 pK units more stable than the uncomplexed benzyl cation. The only pK_{R^+} available for a benzyl cation is that for mesityl cation,[8] and comparison of the pK_{R^+} for the free and complexed cation shows that this complexed benzyl cation is stabilized by 7.7 pK units. Comparison of the rates of solvolysis and pK_{R^+} values shows that the rates reflect the stabilities of the carbonium ions in a well-behaved fashion. This correlation of rates of solvolysis and thermodynamic stabilities of the full cations is usually found[9] and is in sharp contrast to the situation found for the rates of solvolysis of α-ferrocenylcarbinyl derivatives and pK_{R^+} values for the corresponding carbonium ions.[10] The results of Hill and Wiesner indicate that the thermodynamic stabilities of the α-ferrocenylcarbonium ions are much greater than predicted by the kinetic data.[10] This suggests that the stabilizing interactions of the tricarbonylchromium moiety with an arenecarbinyl cation differ from those of the cyclopentadienyliron(II) moiety with a cyclopentadienylcarbinyl cation.

The pK_{R^+} values of several *para*-substituted benzyl cations complexed with tricarbonylchromium were measured and are presented in Table II. A very good correlation exists between these data and σ with $\rho = -5.1 \pm 0.5$. A slightly poorer correlation with σ^+ was obtained with $\rho = -2.7 \pm 0.6$. The better correlation with σ than σ^+ suggests that the interaction of the aromatic π system with the carbonium ion in the complexed cation is much different from that found in the free cation or the effective charge on the benzylic carbon has been greatly diminished by the metal.

Table II. Values of pK_{R^+} for *para*-Substituted Benzyl Cations Complexed with Tricarbonylchromium, π-[p-$ZC_6H_4CH_2$][$Cr(CO)_3$]$^+$

Z	pK_{R^+}
MeO	-10.2
Me	-11.0
H	-11.8
Cl	-12.8

It is interesting to note that the effect of the tricarbonylchromium moiety on the stability of the related tropylium ion is much smaller than it is on that of the benzyl cation. The pK_{R^+} values for tropylium ion and (tropylium)tricarbonylchromium ion are 4.7[11] and 6.3,[2] respectively.

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[8] See Table I, footnote *e*.

[9] See Table I, footnote *b*.

[10] E. A. Hill and R. Wiesner, *J. Am. Chem. Soc.*, **91**, 510 (1969).

[11] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[12] American Chemical Society Petroleum Research Fund Graduate Fellow, 1968–1969.

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Arene–Metal Complexes. II. Thermodynamic Stabilities of α-Substituted α-Hydroxybenzyl Cations Complexed with Tricarbonylchromium. The Variable Cation-Stabilizing Ability of the Tricarbonylchromium Moiety[1]

Sir:

In the first part of this series we reported that benzyl cations are significantly stabilized by complexation with tricarbonylchromium.[1a] In this communication we report the effect of the tricarbonylchromium moiety on stabilities of various α-hydroxybenzyl cations. Of special significance is the fact that some of the tricarbonylchromium-complexed cations are less stable than the free ones.

When ethanol solutions of tricarbonylchromium complexes[2] of benzaldehyde, benzophenone, acetophenone, benzoic acid, and N,N-dimethylbenzamide were injected into highly concentrated (87–97%) sulfuric acid, new ultraviolet–visible spectral absorptions were observed. For example, in water the spectrum of complexed benzaldehyde is 213 (30,400),[6] 267 (5940), 320 (8830), and 423 (3400), and in 94.0% sulfuric acid the spectrum obtained is 210 (21,500), 295 (14,700), 333 (4650), and 453 (3920). When the highly colored solutions of these complexes were poured onto ice, the starting complexed benzoyl compounds were recovered. We interpret these facts to mean that, with the possible exception of the amide which may suffer N-protonation,[7] the complexes undergo reversible O-

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[1] (a) Part I: W. S. Trahanovsky and D. K. Wells, *J. Am. Chem. Soc.*, **91**, 5870 (1969); (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 D. K. W. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

[2] The tricarbonylchromium complexes of benzaldehyde,[3] benzophenone,[4] and benzoic acid[5] were prepared by previously described methods and their melting points agreed with those reported. (Acetophenone)tricarbonylchromium was prepared by the acid-catalyzed hydrolysis of (α-ethoxystyrene)tricarbonylchromium which was prepared by heating the diethyl ketal of acetophenone and hexacarbonylchromium in glyme–butyl ether: mp 86–88° (lit.[5] mp 91.5–92°). The tricarbonylchromium complex of N,N-dimethylbenzamide was prepared by heating the free amide and hexacarbonylchromium in diglyme: mp 96–98°; nmr ($CDCl_3$) δ 5.45 (m, 5) and 3.10 (s, 6). *Anal.* Calcd for $C_{12}H_{11}CrNO_4$: C, 50.53; H, 3.89. Found: C, 50.74; H, 3.93.

[3] G. Drefahl, H.-H. Hörhold, and K. Kühne, *Chem. Ber.*, **98**, 1826 (1965).

[4] J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, **4**, 324 (1965).

[5] B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

[6] The wavelength is in mμ and the molar extinction coefficient is given in parentheses.