The data on methyl radicals[20,23] seem to indicate that this radical reacts with toluenes isoentropically, and a review of the data suggests that all atom transfer processes are approximately isoentropic.[23] If this is true, then the ρ value for any given radical reaction always has the same sign but decreases in absolute value as the temperature is raised.[29] Thus, the positive ρ reported here has significance.

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(28) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 100.

(29) Zavitsas in Figure 1, p 7393, ref 18, uses ρ's at different temperatures; clearly this is unwise.[8]

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A Stable Chromium(IV) Alkoxide of a Secondary Alcohol

Sir:

Extensive evidence of the high oxidative power of chromium(IV) toward organic compounds has been obtained in recent years.[1] In the light of these findings it is not surprising that only a few types of reasonably stable organic chromium(IV) compounds are known: tetraalkoxides,[2] tetrakis(dialkylamides),[3] and tetraalkyls.[4,5]

Until now only tetraalkoxides of tertiary alcohols have been known. Attempts to prepare primary and secondary alkoxides by alcoholysis of tetra-*tert*-butyoxychromium(IV)[2] or tetrakis(dialkylamido)chromium(IV) compounds[3] have been unsuccessful, leading instead to clean oxidation of the alcohol to the corresponding aldehyde or ketone. The mechanism of these oxidations presumably consists of a slow exchange reaction yielding primary or secondary chromium(IV) alkoxides as unstable reaction intermediates which then decompose to chromium(III) species and organic oxidation products.

We now wish to report the preparation of the first stable secondary alkoxychromium(IV) compound, tetrakis(3,3-dimethyl-2-butoxy)chromium(IV). In a typical experiment, 0.5 g of tetra-*tert*-butoxychromium(IV)[6] was added to 6 ml of freshly distilled and degassed pinacolyl alcohol, sealed in an ampoule, and heated in a constant temperature bath at 70° for 36 hr.[7] The contents of the ampoule were transferred to a vacuum line where the alcohols were removed leaving a blue solid; mp 63–64°. *Anal.* Calcd for $C_{24}H_{52}O_4Cr$: Cr, 11.4. Found: Cr, 11.3.

A sample was decomposed with methanol, acidified, and analyzed by nmr; pinacolyl alcohol was the only organic compound (besides methanol) which could be detected. The visible spectrum closely resembles that of the tertiary chromium(IV) alkoxides, with a maximum at 608 nm (ϵ 530) and a shoulder at 730 nm (ϵ 350). The magnetic moment is 3.1 BM.

While tetrakis(3,3-dimethyl-2-butoxy)chromium(IV) is very sensitive to both oxygen and moisture, it is remarkably stable in their absence. A solution of the compound (0.02 *M*) prepared from tetra-*tert*-butoxychromium(IV) and an approximately 150-fold excess of 3,3-dimethyl-2-butanol in dioxane showed less than 1% decomposition over 12 hr at 85°. The pure alkoxide has been stored up to 2 weeks in a sealed flask exposed to normal room light without any apparent decomposition. However, the compound is more sensitive to oxygen and moisture than the *tert*-butoxide. Whereas the latter can be dissolved in methanol giving a blue solution which gradually decays with a measurable rate, the secondary alkoxide reacts almost instantaneously, giving the characteristic reduction product, a gray-green insoluble precipitate which is probably chromium(III) trimethoxide.[8]

The difference in stability of *tert*-butyl methyl carbinolate of chromium(IV) and alkoxides of simple primary and secondary alcohols results from the introduction of bulky *tert*-butyl groups. These groups obviously prevent the molecule from achieving the conformation required for hydrogen transfer in the oxidation step.

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(5) W. Kruse, *ibid.*, **42**, C39 (1972).

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(8) D. A. Brown, D. Cunningham, and W. K. Glass, *J. Chem. Soc. A*, 1563 (1968).

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Site Selection of Metal Complexation in the Semibullvalene Skeleton. The Exigencies of Palladation

Sir:

It has been recently discovered that the semibullvalene skeleton possesses a remarkable capacity to react with transition metal complexes.[1] Tungsten hexacarbonyl and silver nitrate form weak complexes which merely perturb the fluxional system, leaving the basic skeleton unchanged.[2] Diiron nonacarbonyl is more drastic in its action and prefers to insert iron into carbon–carbon σ-bonds, the favored site apparently being the weakest

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(1) For recent work on complex formation with molecules containing the vinylcyclopropane grouping see: A. D. Ketley and J. A. Braatz, *J. Organometal. Chem.*, **9**, 5 (1967); T. Shono, T. Yoshimura, Y. Matsumura, and R. Oda, *J. Org. Chem.*, **33**, 876 (1968); A. Eisenstadt, *Tetrahedron Lett.*, 2005 (1972); R. Aumann, *Angew. Chem.*, **83**, 175, 176, 177 (1971); R. M. Moriarty, C.-L. Yeh, and R. Srinivasan, *Tetrahedron Lett.*, 5325 (1972).

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