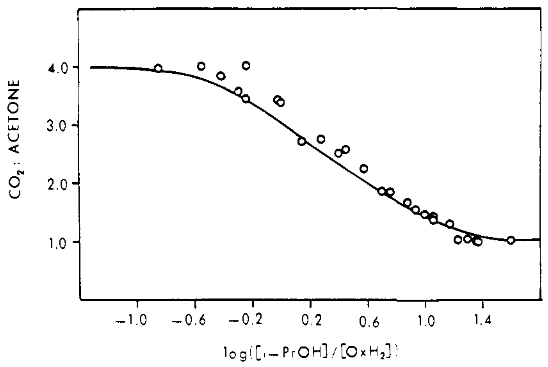

Figure 1. The dependence of the ratio of oxidation products on the substrate ratio in the chromic acid cooxidation of isopropyl alcohol and oxalic acid. The solid line is calculated from eq 9, using the value of $k_5/k_6 = 0.27$.

the total yield of CO_2 is $2(2 - m)$. The experimental CO_2:acetone ratio, x, is given by eq 8 and 9.

$$\frac{CO_2(\text{yield})}{\text{acetone(yield)}} = x = \frac{2(2 - m)}{1 + m} \tag{8}$$

$$x = \frac{(k_5/k_6)([R_2CHOH]/[CO_2H]) + 2}{(k_5/k_6)([R_2CHOH]/[CO_2H]) + 0.5} \tag{9}$$

Equation 10 (from eq 7 and 8) relates the ratio of reaction products to the ratio of the concentrations of the substrates

$$\frac{4 - x}{2(x - 1)} = \frac{k_5}{k_6}\frac{[R_2CHOH]}{[(CO_2H)_2]} \tag{10}$$

Plotting the data from Table I according to eq 10, one obtains a reasonably good straight line (Figure 2), with a slope $k_5/k_6 = 0.27$. Oxalic acid is thus about 3.7 times more reactive toward chromium(V) than isopropyl alcohol.

This approach is of general utility and will permit the determination of the reactivity of a variety of compounds, relative to oxalic acid, toward chromium(V), provided that they can participate in a cooxidation reaction with oxalic acid similar to isopropyl alcohol.[2]

It is interesting to compare the relative reactivities of the two substrates, oxalic acid and isopropyl alcohol, toward chromium(V) and chromium(VI). Under conditions comparable to these reactions in which chromium(V) reacts 3.7 times faster with oxalic acid than with isopropyl alcohol, chromium(VI) is about 120 times more reactive.[5] The higher reactivity of chromium(VI) toward oxalic acid is most likely due to the availability of the three-electron oxidation mechanism[1] for the latter reaction.

It should be noted that in Figures 1 and 2 all points lie on single lines, regardless of acidity.[6] One can thus conclude that the chromium(V) oxidations of both alcohols and of oxalic acid exhibit the same dependence on acidity. As the chromium(V) oxidation of oxalic acid is independent of acidity,[7] it follows that the chromium(V) oxidation of isopropyl alcohol is also acidity independent within the acidity region covered by the present study. In this respect, the chromium(V) oxidation of isopropyl alcohol differs significantly from the chromium(VI) oxidation, which is well known to be acid catalyzed.[8]

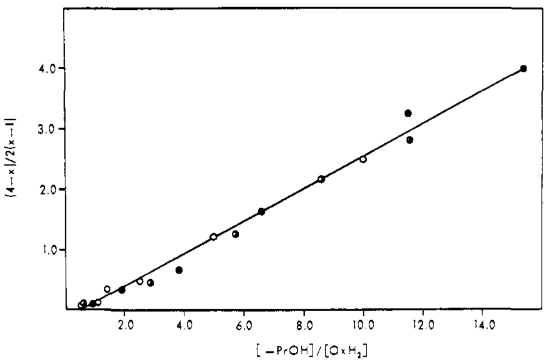

Figure 2. Determination of the relative rates of chromium(V) oxidation of isopropyl alcohol and oxalic acid–perchloric acid: (○), 0.063 *M;* (●), 0.125 *M;* (◑), 0.63 *M.*

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[5] In 0.097 *M* perchloric acid, the rate of reduction of chromium(VI) by 0.10 *M* isopropyl alcohol is 1.41×10^{-5} sec^{-1} and by 0.097 *M* oxalic acid is 1.70×10^{-3} sec^{-1}.

[6] This is true only provided that undissociated oxalic acid, rather than the total analytical concentration of oxalic acid, is taken into account. This indicates that only undissociated oxalic acid is kinetically active as a reducing agent toward chromium(V). This conclusion parallels our reported findings for chromium(VI).[1]

[7] V. Srinivasan and J. Roček, unpublished results.

[8] F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).

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Generation and Reactions of Anions α to the Carbene Carbon Atom of Transition Metal–Carbene Complexes

Sir:

Since stable metal–carbene complexes were first characterized by Fischer[1] in 1964, these complexes have attracted much interest as possible reagents for organic synthesis. To realize this possibility, synthetically useful ways of releasing the carbene ligand from the metal complex and efficient syntheses of a wide variety of metal–carbene complexes must be found. In an attempt to solve the first problem, we recently reported the reaction between metal–carbene complexes and Wittig reagents which gives high yields of vinyl ethers.[2] Here we report the reactions of anions generated α to the carbene carbon atom with electrophilic reagents which allow elaboration upon the structure of simple metal–carbene complexes.

Protons attached to the α-carbon atom in metal–carbene complexes undergo rapid base-catalyzed hydrogen–deuterium exchange with hydroxylic solvents.[3] For instance, the half-life for exchange of the α protons in **1** in acetone-D_2O with no added base is 23 min at 40°.[4] This rapid exchange implies the existence of an intermediate carbanion.

We have now been able to generate solutions of these anions at low temperature in ether solvents. Treatment of a light yellow tetrahydrofuran solution of 50 mg of the cyclic metal–carbene complex **1**[4] at −78°

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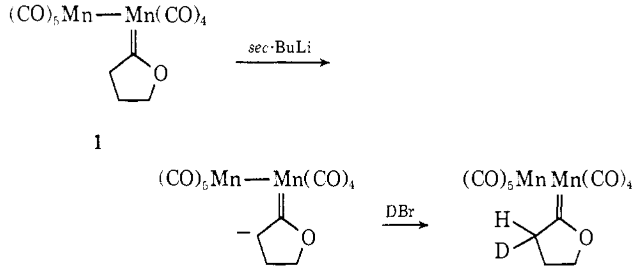
[1] E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, 3, 580 (1964); *Chem. Ber.*, 100, 2445 (1967).

[2] C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, 94, 6543 (1972).

[3] C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, 7, 390 (1968).

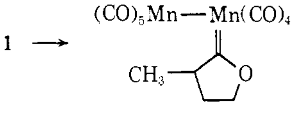
[4] C. P. Casey, *Chem. Commun.*, 1220 (1970).



1

with 1 equiv of *sec*-butyllithium in hexane resulted in the immediate formation of a deep red solution. Quenching the solution with DBr in CH_3OD (90% D) returned the solution to its original light yellow color. Evaporation of solvent and sublimation of the residue gave 25 mg of **1** (50% recovery). Mass spectra of recovered **1** indicated that it was a mixture of 4% d_2, 84% d_1, and 12% d_0 material. Similarly when a light yellow tetrahydrofuran solution of 50 mg of (methylmethoxycarbene)pentacarbonyltungsten(0)[1] (**2**) was treated with 1 equiv of *n*-BuLi in hexane a red-brown solution was produced. The solution was quenched by injection into a rapidly stirred solution of DCl in ether. After evaporation of the solvent and sublimation, 18 mg (35%) of **2** was recovered. In this case partial scrambling of deuterium in the carbene complex could not be prevented and the mass spectrum indicated a mixture of 0.5% d_3, 11.3% d_2, 69.5% d_1, and 18.7% d_0 material.

Alkylation of the anions α to the carbene carbon atom has been achieved with methyl fluorosulfonate. Treatment of 100 mg of **1** in THF with 1 equiv of *sec*-butyllithium at −78° followed by 1 equiv of methyl fluorosulfonate gave a yellow solution from which 47 mg of the methylated product **3**, mp 65–67°, was isolated by thick layer chromatography on silica gel. **3** was identified by spectral properties: mol wt (high-resolution mass spectrometry) 445.8860 (calcd for $Mn_2C_{14}H_8O_{10}$, 445.8877); $\nu_{max}^{heptane}$ 1941 (m), 1952 (m), 1963 (m), 1980 (vs), 1990 (vs), 2002 (m), 2018 (s), 2078 (m) cm^{-1}; $\delta_{TMS}^{benzene}$ 0.80 (d, J = 8 Hz, 3 H), 0.80–1.30 (m, 2 H), 3.0–4.2 (m, 3 H). **3** was also independently synthesized from 4-chloro-2-methylbutyryl chloride and $NaMn(CO)_5$ by a procedure similar to that used to prepare **1**.[4] Similarly, reaction of the anion generated from the tungsten–carbene complex **2** with methyl fluorosulfonate gave a 40% yield of (ethylmethoxycarbene)pentacarbonyltungsten(0) (**4**): mp 10°; mol wt (mass spectrum) 395.9840 (calcd for $WC_9H_8O_6$, 398.9830); $\nu_{max}^{heptane}$ 2072 (w), 1983 (s), 1960 (s), 1947 (s) cm^{-1}; $\delta_{TMS}^{CS_2}$ 4.58 (s, 3 H), 3.22 (q, J = 7.3 Hz, 2 H), 1.03 (t, J = 7.3 Hz, 3 H). **4** was independently synthesized using the method of Fischer[1] from $W(CO)_6$ and ethyllithium.



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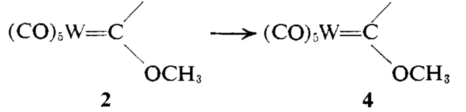
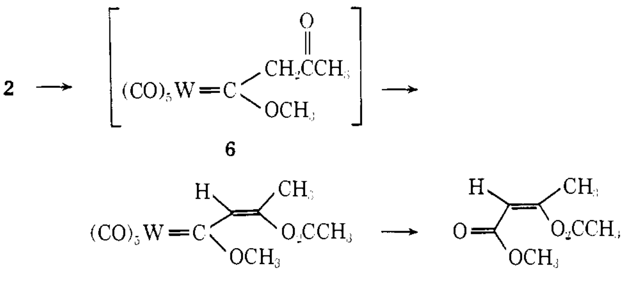


2 4

Anions generated α to the carbene carbon of metal–carbene complexes react with aldehydes to give condensation products. The anion of **2** (1.0 g, 2.68 mmol) was generated from 1 equiv of *n*-butyllithium in diethyl ether at 0° and was treated with benzaldehyde. The reaction mixture was purified by column chromatography using a silica gel–pentane system to give 0.24 g (19% yield) of dark red solid which was further purified by low-temperature crystallization from pentane and sublimation at 60° (0.005 mm) to give (*trans*-styrylmethoxycarbene)pentacarbonyltungsten(0) (**5**): mp 84.5–86°; mol wt (mass spectrum) 469.9990 (calcd for $WC_{15}H_{10}O_6$ 469.9987); $\nu_{max}^{heptane}$ 2073 (m), 2066 (w), 1975 (w), 1951 (s), 1939 (vs) cm^{-1}; $\delta_{TMS}^{acetone\text{-}d_6}$ 4.70 (s, 3 H), 8.03 (d, J = 16 Hz, 1 H), 7.50 (m, 5 H), 7.35 (d, J = 16 Hz, 1 H). *Anal.* Calcd for $WC_{15}H_{10}O_6$: C, 38.33; H, 2.15; W, 39.11. Found: C, 38.43; H, 1.99; W, 39.26.

Treatment of **5** with ceric ammonium nitrate[2] in acetone effected conversion to methyl *trans*-cinnamate in quantitative yield.

Reaction of the anion of **2** with acetyl chloride does not give the simple acetylated product **6** but does allow the isolation of the enol acetate **7** derived from **6**.



6

7 8

Treatment of 500 mg of **2** in tetrahydrofuran at −20° with 1 equiv of *n*-butyllithium gave a red-brown solution of the anion of **2**. Reaction of this solution with 2 equiv of acetyl chloride and separation by preparative thick layer chromatography gave 31% recovery of **2** and 23% of a new red crystalline material, mp 97–102°, which we formulate as a 2:1 mixture of [(*Z*)- and (*E*)-(2-acetoxy-1-propenyl)methyoxycarbene]pentacarbonyltungsten(0) (**7**). The molecular weight of **7** was determined by mass spectroscopy to be 465.9875 (calcd for $WC_{12}H_{10}O_8$, 465.9885). The nmr spectrum indicated that **7** was a 2:1 mixture of isomers. The nmr (CS_2) of the major isomer had resonances at δ 2.05 (d, J = 1 Hz, 3 H, $CH_3C{=}C$), 2.13 (s, 3 H, CH_3CO_2), 4.61 (s, 3 H, $\text{-}OCH_3$), and 7.34 (q, J = 1 Hz, 1 H, $HC{=}C$), while the minor isomer had resonances at 1.89 (d, J = 0.8 Hz, 3 H, $CH_3C{=}C$), 2.07 (s, 3 H, CH_3CO_2), 4.49 (s, 3 H, OCH_3), and 6.94 (q, J = 0.8 Hz, 1 H, $HC{=}C$). The major isomer is tentatively assigned the *E* configuration about the carbon–carbon double bond since the vinyl proton appears 0.38 ppm further downfield than the vinyl proton in the minor isomer due to the deshielding effect[5] of the cis acetoxy group. The infrared spectrum of the mixture had absorptions for metal carbonyls at 2066 (m), 1984 (m), and 1946 (s) cm^{-1}, for the acetate carbonyl at 1770 cm^{-1}, and for the carbon–carbon double bond at 1602 cm^{-1}.

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(5) H. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963).

The structure of **7** was confirmed by oxidation with ceric ammonium nitrate in 80% acetone–20% H_2O, a reagent known[2] to cleave methoxycarbene complexes to methyl esters, which gave a 2:1 mixture of methyl 2-acetoxy-2-butenoate (**8**). The nmr (CCl_4) of the major isomer of **8** had resonances at δ 1.98 (d, J = 1.1 Hz, 3 H, $CH_3C{=}C$), 2.15 (s, 3 H, CH_3CO_2), 3.62 (s, 3 H, OCH_3), and 5.58 (m, 1 H), while the minor isomer had resonances at δ 2.10 (s, 3 H, CH_3CO_2), 2.32 (br s, 3 H, $CH_3C{=}C$), 3.67 (s, 3 H, OCH_3), and 5.60 (m, 1 H, $HC{=}C$).[6] The major isomer of **8** obtained from ceric oxidation is assigned the *E* structure on the basis of the greater downfield chemical shift of the vinyl proton of the major isomer.[5]

The results presented here indicate that anions α to the carbene carbon atom of transition metal–carbene complexes are versatile intermediates for the synthesis of a wide variety of transition metal–carbene complexes.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. GP-32160).

[6] An authentic sample of **8** was prepared from methyl acetoacetate and isopropenyl acetate and was shown by gas chromatography to be a 1:24 mixture of the major and minor isomers obtained above.

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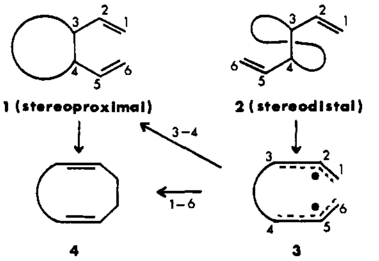
The Stereodistal Cope Rearrangement of *trans*-1,2-Dialkenylcyclobutanes[1]

Sir:

Although stereoproximity of the ends (C_1 and C_6) of the biallyl system (schematically shown as **1**) is required in the ordinary Cope rearrangement, there are a number of cases in which the process occurs despite a stereodistal relationship (**2**) imposed by the geometry of the reactant.[2a,b] A major mechanistic question is does the stereodistal[2c] reaction occur by an indirect mechanism requiring prior epimerization to the stereoproximal reactant, perhaps by way of a diradical intermediate **3**, or can it occur directly, for example by closure of **3** at C_1 and C_6, to give Cope rearrangement product **4**?

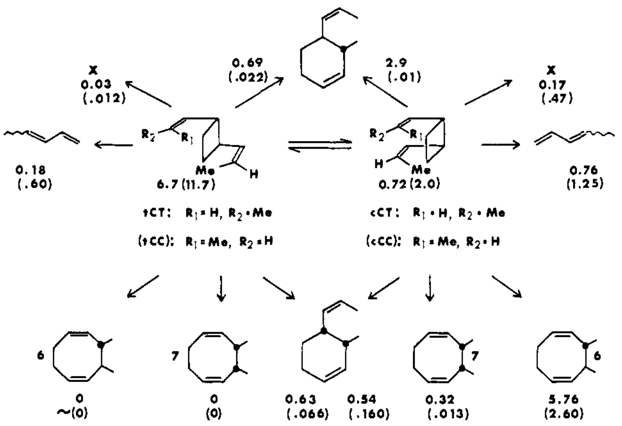


In one previously discussed example of this problem, the thermal rearrangement of *trans*-1,2-divinylcyclobutane (tDV) to cycloocta-1,5-diene (**5**),[3–6] evaluation of the indirect mechanism on energetic grounds does not seem to be straightforward. There are two conflicting thermochemical estimates (~0[5] and ⩾7.6[6] kcal/mol) of the activation energy for cyclization of the octa-1,7-diene-3,6-diyl diradical, the hypothetical precursor of **5**. Moreover, the question is difficult to test experimentally with tDV because the stereoproximal intermediate, *cis*-1,2-divinylcyclobutane (cDV), rearranges to **5** too rapidly.[3]

This paper reports a circumvention of this difficulty in two related stereodistal systems, *trans*-1,2-*cis,trans*- and *trans*-1,2-*cis,cis*-dipropenylcyclobutanes (tCT and tCC, Scheme I). These are especially well suited for the detection of the indirect mechanism because the Cope rearrangements of the corresponding stereoproximal compounds, cCT and cCC, are known[7] to be much slower (factors of 2×10^{-3} and 5×10^{-6}, respectively) than that of cDV. In fact, we now find that cCT and cCC accumulate during pyrolyses of tCT and tCC, respectively, at 146.5°, and both reactions are reversible. Although consistent with the indirect mechanism, these observations do not exclude contributions from the direct one. The relative importance of the two paths, however, can be evaluated by a kinetic analysis of the tCT–cCT and tCC–cCC systems.

Scheme I shows the products formed (capillary vapor chromatographic analysis) in the reactions at 146.5° of degassed neat liquid samples of each of these four compounds. With the exception of the 1–6% of unidentified components (X, Scheme I), all of the products are stable under the reaction conditions.

Scheme I



Because of trans ⇌ cis reversibility, the pyrolyses do not follow first-order kinetics, but the kinetic scheme can be solved numerically. Early points in the kinetic runs provide approximate values of the rate constants.

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[1] We thank the National Science Foundation (Grant No. GP-33909X) and the Hoffmann-La Roche Foundation for partial support of this work.

[2] (a) For an early example, see *trans*-divinylcyclopropane → cyclohepta-1,4-diene: E. Vogel, *Angew. Chem.*, **72**, 4 (1960). (b) See also C. Ullenius, P. W. Ford, and J. E. Baldwin, *J. Amer. Chem. Soc.*, 94, 5410 (1972). (c) Stereodistal and stereoproximal Cope reactants are related by configurational inversion at C_3 or C_4 of the biallyl system.

[3] G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).

[4] D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).

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[6] W. von E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *J. Amer. Chem. Soc.*, 94, 3833 (1972).

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