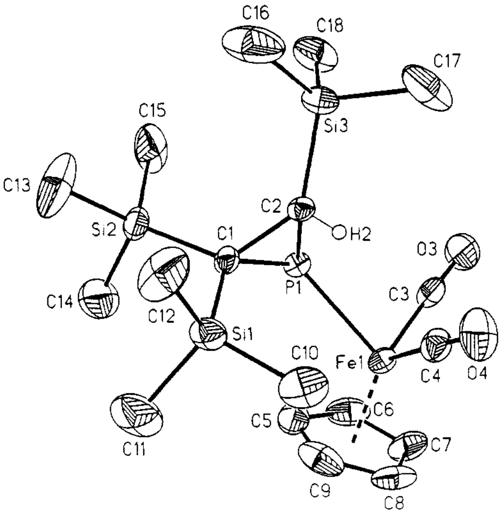

Figure 1. Structure of **2a**, showing one independent molecule and the atomic numbering scheme with ellipsoids at the 30% probability level. Important bond lengths (pm) and angles (deg) of **2a** (bond lengths and angles of the other molecule in the asymmetric unit are in brackets): P(1)–Fe(1) 233.1 (2) [234.5 (2)], P(1)–C(1) 187.2 (7) [188.6 (7)], P(1)–C(2) 186.1 (6) [185.6 (6)], C(1)–C(2) 155.4 (9) [156.5 (9)], C(1)–Si(1) 189.2 (8) [189.0 (8)], C(1)–Si(2) 189.9 (8) [191.2 (8)], C(2)–Si(3) 186.9 (7) [187.0 (7)]; Fe(1)–P(1)–C(1) 123.5 (2) [123.5 (3)], Fe(1)–P(1)–C(2) 117.6 (2) [116.0 (2)], C(1)–P(1)–C(2) 49.2 (3) [49.5 (3)], P(1)–C(1)–C(2) 65.0 (3) [64.3 (3)], P(1)–C(2)–C(1) 65.8 (3) [66.2 (3)].

spectra, and by a single-crystal determination of **2a**.[7] Compared with the $\delta(^{31}P)$ values of a series of corresponding P-substituted phosphiranes, $R\overline{PCH(SiMe_3)C}(SiMe_3)_2$ (δ −20.2 to −245.0),[5] the resonances of **2a–c** (δ −59.7 (**2a**), −30.6 (**2b**), −64.9 (**2c**)) are observed in the "low field" range. This reflects a higher degree of s character of the phosphorus–carbon bonds, as is also shown by the large values for the coupling constants in **2a–c** (J_{PC} = 64–89 Hz) compared with corresponding organo-substituted derivatives.[5] The constitution of **3** was inferred from its mass spectrum[8] and ^{31}P NMR data. The presence of the second λ^3-phosphirane complex **3** is indicated by the characteristic high-field ^{31}P resonance with a doublet of doublets pattern (δ −119.2, $^1J_{PH}$ = 366.7 Hz, $^2J_{PH}$ = 5.2 Hz).

The structure of **2a** is illustrated in Figure 1. The P–C bonds (187 pm) in the triangle correspond to a bond order of unity, whereas the C–C distance (156 pm) is considerably lengthened. This results in a widening of the PCC angles (65°), whereas the CPC intracyclic angle is very small (49°). A similar bonding situation is observed for the λ^3-phosphirane $Ph\overline{PCPh_2C}(SiMe_3)_2$.[9] However, in contrast to known λ^3-phosphiranes[1] the exocyclic angles at phosphorus are widened (120°) due to the presence of the bulky organometallic substituent. This indicates a high degree of s character in the Fe–P bond. The bond length itself (234 pm) is comparable to those in the P-metalated diphosphirane $(\eta^5\text{-}C_5H_5)Fe(CO)_2PP(^tBu)C(Ph)SiMe_3$[2b] and 1,2-diphosphaspiro[2.2]pentane $(\eta^5\text{-}C_5Me_5)Fe(CO)_2PP\text{-}(2,4,6\text{-}^tBu_3C_6H_2)CCH_2CH_2$.[2a]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Registry No. 1, 124489-76-5; **2a**, 136947-57-4; **2b**, 136947-58-5; **2c**, 136947-59-6; **3**, 136947-60-9; 4, 136947-55-2; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]K$, 60039-75-0; $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]K$, 59654-59-0; $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3]K$, 136947-56-3; $(MeCN)_3Mo(CO)_3$, 15038-48-9; $[HFe(CO)_4]Na$, 53558-55-7; $K[C_5Me_5]$, 94348-92-2.

Supplementary Material Available: Tables of atomic coordinates and isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters (7 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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(7) Single crystals of **2a** were obtained by low-temperature crystallization from pentane. The data were collected at ambient temperature on a Nicolet R3m four-circle diffractometer (ω-scan mode, Mo Kα radiation, λ = 71.069 pm) and solved and refined with SHELXTL and SHELXTL-PLUS, respectively. Compound **2a**, $C_{18}H_{33}FeO_2PSi_3$, M_r = 452.5, crystallizes in space group $P2_1/n$ (No. 14), with a = 1466.8 (5) pm, b = 1774.7 (5) pm, c = 1912.3 (9) pm, β = 97.11 (4)°, V = 4.940 nm^3, Z = 8, D_{calc} = 1.22 g cm^{-3}, μ(Mo Kα) = 0.82 mm^{-1}, and $F(000)$ = 1920. A total of 6476 unique reflections were recorded, of which 2755 were considered as unobserved [$F < 4\sigma(F)$], leaving 3721 for solution and refinement (451 parameters). The final residuals were R = 0.059 and R_w = 0.054 with weighting scheme $w^{-1} = \sigma^2(F) + gF^2$ (g = 0.0005). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were localized by a difference electron density determination and refined using a "riding" model.

(8) MS (EI, 70 eV, m/e (relative intensity)): 444 (2, M$^+$), 416 (3, M$^+$ − CO), 388 (2, M$^+$ − 2CO), 360 (8, M$^+$ − 3CO), 322 (28 (M$^+$ − 4CO), 73 (100, $SiMe_3$).

(9) Appel, R.; Gaitzsch, T.; Knoch, F.; Lenz, G. *Chem. Ber.* **1986**, *119*, 1977.

Thermal Reaction of Chromium (Acyloxy)carbene Complexes: Synthesis of Enol Esters

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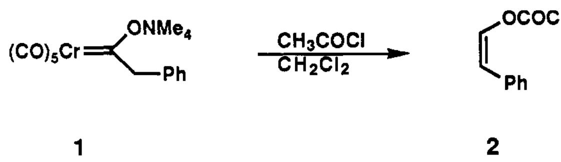
Received July 11, 1991

Summary: Reaction of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes with acyl chlorides at −40 °C followed by slow warming to ambient temperature affords exclusively or predominantly *Z* enol esters in moderate to good yield.

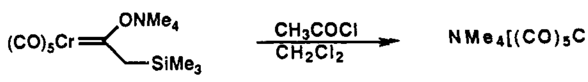
A number of synthetically useful reactions of alkoxy and amino Fischer carbenes, especially those of chromium, have been developed since their discovery almost 30 years ago. Compounds with a variety of structures such as cyclobutanones, β-lactams, cyclopropanes, amino acids, and fused aromatic systems can be prepared by utilizing these reagents.[1]

Scheme I



0276-7333/91/2310-3951$02.50/0 © 1991 American Chemical Society

Scheme II



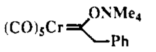
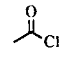
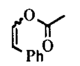
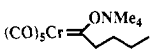
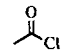
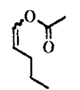
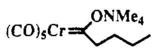
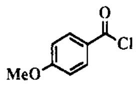
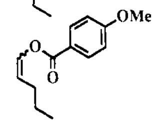
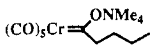
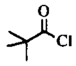
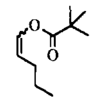
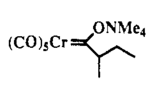
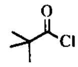
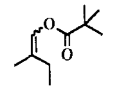
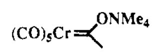
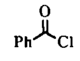
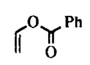
3 **4**

(Acyloxy)carbenes, apart from being used as intermediates in the synthesis of other heteroatom-substituted complexes such as alkoxy- and aminocarbenes, have received little attention, most likely due to their high thermal instability.[2] Chromium and molybdenum (acyloxy)carbenes rapidly decompose at room temperature, as do their tungsten counterparts at 50 °C.[3] To our knowledge, pentacarbonyl[(acyloxy)(2-furyl)carbene]chromium(0) is the only acyl chromium complex reported to be stable at ambient temperature.[2b]

Wulff and co-workers have published two reactions of chromium (acyloxy)carbenes, one affording cyclopropanes in the presence of enol ethers[4] and one forming a new iminocarbene together with an *O*-acyl imidate by reaction with imines.[5] Although the thermal decomposition of chromium (acyloxy)carbenes is well-known, it has been little studied and no major organic products have been isolated.[2c,6]

We describe herein a new reaction of chromium (acyloxy)carbenes having a hydrogen α to the carbene carbon. Thus, reaction of a methylene chloride solution (30 mL) of tetramethylammonium pentacarbonyl(1-oxy-2-phenylethylidene)chromate(0) (**1**; 2 mmol) with 1 equiv of acetyl chloride, at -40 °C under a nitrogen atmosphere, followed by slow warming (overnight) to ambient temperature gave a faint yellow solution with a yellow precipitate. Removal of the solvent, on a rotary evaporator at water aspirator pressure, followed by chromatography on a short silica gel column (hexane) afforded (*Z*)-2-phenyl-1-ethen-1-ol acetate (**2**) in 70% yield (Scheme I). Alkoxycarbenes have been shown to undergo, at elevated temperatures in the presence of pyridine, a similar elimination reaction to give predominantly *Z* enol ethers.[7]

Table I. Enol Esters from Tetramethylammonium Pentacarbonyl(1-oxyalkylidene)chromate(0) Complexes

Complex[a,b]	Acid Chloride	Product	Yield[c]
			70% *Z*/*E*, >20:1
			5% *Z*/*E*, >20:1
			79% *Z*/*E*, 15:1
			49% *Z*/*E*, 6:1
			45% *Z*/*E*, 3:2
			38%

[a] The reactions were performed with isolated complexes prepared by addition of an organolithium to a slurry of Cr(CO)$_6$ in Et$_2$O followed by addition of Me$_4$NCl. [b] All reactions performed as described in text. [c] Refers to pure compounds isolated by chromatography or distillation.

In addition to the organic product, an essentially quantitative yield of NMe$_4$[(CO)$_5$CrCl] (**4**) was isolated. The latter product has been obtained by Connor and Jones in a similar reaction of the tetramethylammonium pentacarbonyl(1-oxy-2-(trimethylsilyl)ethylidene)chromate(0) complex **3** with acetyl chloride in methylene chloride (Scheme II).[6] We believe that an enol ester product was formed in this reaction but may have been lost during workup due to its high volatility.

Enol esters have proven to be valuable intermediates in organic synthesis, and several methods are available for their preparation. Commonly used methods include base or acid treatment of aldehydes or ketones with an appropriate acid anhydride or chloride, addition of carboxylic acids to alkynes, and palladium-promoted acetoxylation of alkenes.[8] Unfortunately, very few methods exist, to our knowledge, to prepare these esters with high regioselectivity.[8b,9]

Enol esters were shown to be the only organic product, in fair to good yield, from a selection of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes, all containing a hydrogen α to the carbene carbon. Although the material balance in most cases is fair, the enol esters are the only organic products seen during (GLC) or after the reaction (NMR). All four acid chlorides examined, acetyl chloride, trimethylacetyl chloride, benzoyl chloride, and 4-methoxybenzoyl chloride, gave enol ester products (Table I).[10] In addition to the 2-phenylethylidene complex (entry 1 in Table I), high isomeric purity ($Z/E > 20/1$, GLC and ^{1}H NMR) of the *Z* enol ester[11] was also obtained from the reaction of tetra-

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(1) For a recent example and pertinent references, see the following. (a) Cyclobutanones: Hegedus, L. S.; Bates, R. W.; Söderberg, B. C. *J. Am. Chem. Soc.* **1991**, *113*, 923. (b) Cyclopropanes: Hegedus, L. S.; Söderberg, B. C. *Organometallics* **1990**, *9*, 3113. (c) Amino acids: Hegedus, L. S.; Schwindt, M. A.; DeLombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264. (d) β-Lactames: Hegedus, L. S.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1109. (e) Fused aromatics: Dötz, K. H.; Popall, M.; Müller, G.; Ackermann, K. *J. Organomet. Chem.* **1990**, *383*, 93. For recent reviews on Fischer carbene chemistry, see: (f) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (g) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (h) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Eds.; JAI Press: Greenwich, CT, 1989; Vol 1. (j) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, England, 1990; Vol. 5.

(2) (a) Fischer, E. O.; Heckl, B.; Dötz, K. H.; Müller, J. *J. Organomet. Chem.* **1969**, *16*, P29. (b) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 1974. (c) Wulff, W. D.; McCallum, J. S.; Kunng, F.-A. *J. Am. Chem. Soc.* **1988**, *110*, 7419.

(3) Fischer, E. O.; Selmayer, T.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 2947.

(4) Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660.

(5) Murray, C. K.; Warner, B. P.; Dragisch, V.; Wulff, W. D.; Rogers, R. D. *Organometallics* **1990**, *9*, 3142.

(6) Connor, J. A.; Jones, E. M. *J. Organomet. Chem.* **1973**, *60*, 77.

(7) (a) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642. (b) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. (c) Casey, C. P.; Brunsvold, W. R. *Inorg. Chem.* **1977**, *16*, 391. (d) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. (e) Fischer, E. O.; Maasböl, A. *J. Organomet. Chem.* **1968**, *12*, P15.

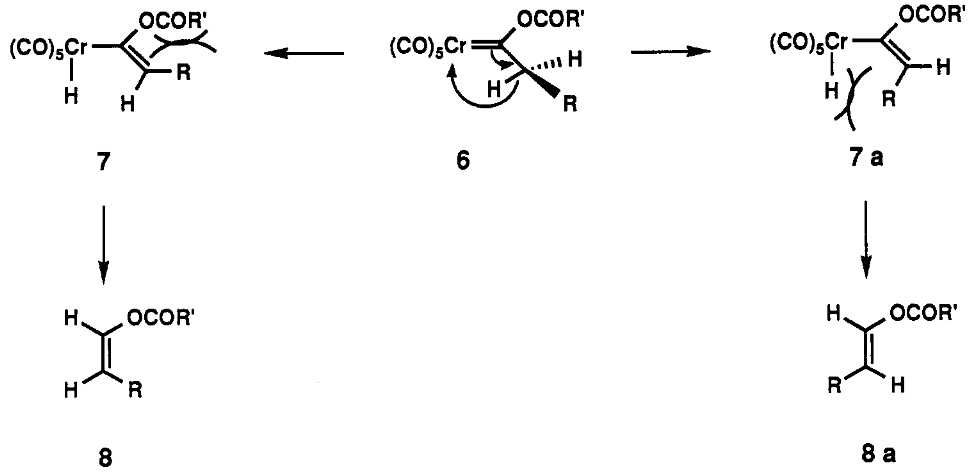
(8) (a) Larock, R. C. *Comprehensive Organic Transformations*; VCH Publishers: New York, 1989. (b) For an extensive list of references for the preparation and reaction of enol esters, see also: Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966.

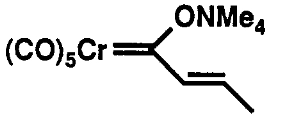
(9) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993.

(10) The products readily hydrolyze after a few weeks upon storage at -18 °C. The enol ester products in entry 5 were shown to hydrolyze more rapidly, and a correct elemental analysis could not be obtained.

(11) Cousineau, T. J.; Cook, S. L.; Secrist, J. A., III. *Synth. Commun.* **1979**, *9*, 157.

Scheme III





5

Figure 1.

methylammonium pentacarbonyl(1-oxypentylidene)chromate(0) with acetyl chloride (entry 2), although in very low chemical yield. To compare the influence of size of the electrophile on the stereochemical outcome of the reaction, 4-methoxybenzoyl chloride and trimethylacetyl chloride were reacted with tetramethylammonium pentacarbonyl(1-oxypentylidene)chromate(0) (Table I). Apparently, an increase in the size of the electrophile affords a lower Z/E ratio, as seen in going from the least bulky acetyl chloride to 4-methoxybenzoyl chloride ($Z/E = 15/1$) to trimethylacetyl chloride ($Z/E = 6/1$). Performing the reaction with the same chromium complex and trimethylacetyl chloride under identical conditions but in the present of pyridine, conditions known to accelerate the formation of enol ethers from alkoxycarbenes,[7] gave a comparable yield (45%) of product with a slightly higher Z/E ratio (9/1). The reason for this higher stereoselectivity, in the presence of pyridine, is presently not known.

The isomeric esters were easily distinguished by ^{1}H NMR spectroscopy. Relatively small H–H coupling constants, J = 8.0, 7.0, 6.4, and 6.4 Hz (entries 1–4, respectively), were observed across the double bond typical for a cis configuration of protons, whereas the same coupling constant for the minor E enol ester (entry 3) is 12.5 Hz.[12] A trisubstituted enol ester was obtained upon reaction of the α,α-disubstituted complex in entry 5 with trimethylacetyl chloride. The product was tentatively assigned, by ^{1}H NMR spectroscopy, as a 3/2 mixture of Z to E isomers. The vinylic methyl group of the E isomer has a resonance at δ 1.63 ppm shifted upfield (0.05 ppm) compared to the Z isomer.[13] As a final example, vinyl benzoate was isolated in 38% yield, from the reaction of tetramethylammonium pentacarbonyl(1-oxyethylidene)chromate(0) with benzoyl chloride (entry 6). For obvious reasons, complexes lacking an α-hydrogen do not give enol esters; moreover, only very small amounts of alkyne products (<5%) have been isolated from thermal decomposition of such complexes.[2c] The propenylidene complex **5** (Figure 1), having a vinylic α-hydrogen, did not afford any organic product upon reaction with trimethylacetyl chloride, although the starting material was completely consumed.[14]

A possible mechanism for the formation of the enol esters is depicted in Scheme III. Acylation of a tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complex affords the unstable (acyloxy)carbene **6**. β-hydrogen elimination gives either of the (σ-alkyl)chromium hydride species **7** of **7a**. Two main steric interactions are to be expected in complexes of this structure, interactions either between the alkyl group in **7a** and chromium-bound hydride or carbonyl ligands (shown for the hydride in Scheme III) or between the alkyl group and the ester moiety in **7**. In all cases the carbonyl ligands and the hydride are more sterically demanding in comparison to the ester group; thus, β-elimination to the less sterically congested intermediate **7** is preferred. Reductive elimination from **7** or **7a** forms the products **8** and **8a**, respectively, and completes the reaction sequence. Increasing the size of the ester group should, according to this mechanism, decrease the Z/E ratio, which was experimentally observed (entry 2–4).

In summary, a procedure for the synthesis of enol esters by thermal decomposition of in situ formed pentacarbonyl[1-(acyloxy)alkylidene]chromium(0) complexes, generated by electrophilic attack of acyl chlorides upon tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes, has been developed. Further studies of the mechanism, scope, and synthetic utility of this novel reaction are currently underway in our laboratories.

Acknowledgment. This research was supported by an award from Research Corp. We also thank Dr. Aladar Bencsath for mass spectra.

Supplementary Material Available: Spectral data for all new enol esters (entries 3–5 in Table I) (2 pages). Ordering information is given on any current masthead page.

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(12) (Z)-2, J = 8.0 Hz; (E)-2, J = 12.5 Hz: Yamane, T.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Tetrahedron* **1973**, 955.

(13) For similar shifts of related compounds see: (a) House, H. O.; Kramar, V. *J. Org. Chem.* **1963**, *28*, 3362. (b) Wasserman, H. H.; Keller, L. S. *Tetrahedron Lett.* **1974**, 4355.

(14) Some chromium hexacarbonyl was isolated after chromatography of the crude reaction mixture.