proximately 1.3×10^4 M^{-1} s^{-1}. Similar treatment using eq 5 and the data from Table II give the respective k_5^2/k_4 ratios and estimated k_5 values: for $CHCl_3$, $k_5^2/k_4 = (1.2 \pm 0.2) \times 10^{-7}$ M^{-1} s^{-1} and $k_5 \simeq 21$ M^{-1} s^{-1}; for $PhCH_2Cl$, $k_5^2/k_4 = (5.5 \pm 2) \times 10^{-8}$ M^{-1} s^{-1} and $k_5 \simeq 14$ M^{-1} s^{-1}; for CH_2Cl_2, $k_5^2/k_4 < 10^{-10}$ M^{-1} s^{-1} and $k_5 < 0.6$ M^{-1} s^{-1}.

The reactivity order observed here for the trapping of the metal radical by the various chlorocarbons has analogy in other examples of halogen abstraction from halocarbons. For example, rates of bromine atom abstraction as illustrated in eq

$$R'\cdot + R''\text{-Br} \rightarrow R'\text{-Br} + R''\cdot \quad (6)$$

6 have been reported for cases where R'· is the methyl radical[19] or where R'· is the tri-*n*-butyltin radical[20] in hydrocarbon solvents. In both cases, the relative reactivities for the trapping agents R''Br followed the order $CCl_3Br > CHCl_2Br > PhCH_2Br > CH_2ClBr$. Also, for the tri-*n*-butyltin radical, chloride abstraction from CCl_4 is about three orders of magnitude faster than from $PhCH_2Cl$.[20] Other chloride abstractions analogous to eq 6 display similar orders of halocarbon reactivities. The gas-phase chlorine atom abstraction from the chloromethanes by sodium atoms displays a strong dependence on the number of chlorines $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$ with each chlorine increasing the rate by roughly an order of magnitude.[21] A closer analogy to the present case is the use of chromium(II) as a reducing agent in mixed aqueous solvents.[22,23] With the chloromethanes, the rate of chloride abstraction by Cr(II) follows the order seen with the gas-phase sodium atom reaction.[23] Furthermore, comparison of the Cr(II) reductions of $CHCl_3$ and $PhCH_2Cl$ under somewhat different conditions ($CHCl_3$ in 29.8 °C, 50% aqueous dimethylformamide;[23] $PhCH_2Cl$ in 27.5 °C, 22% aqueous ethanol[22]) indicates that chloroform is an order of magnitude the more reactive.

In summary, the proposed model (Scheme I) provides a reasonable explanation of the variations of Φ_d measured for the irradiation of $[\pi\text{-CpW(CO)}_3]_2$ in THF solution containing different concentrations of the halocarbon trapping agents. The quantum yield data demonstrate that the metal radicals produced display considerable selectivity in their chemical reactions. This selectivity includes the failure to abstract hydrogen from solvent, various reactivities with chlorocarbon trapping agents in a manner consistent with other radicals, and much more rapid reaction with another radical to re-form the starting material. In addition, it is clear that the quantum yields observed in the different chloromethane solvents do not reflect simply the ease of chlorine abstraction from the solvent trapping agent and instead indicate solvent effects on the primary quantum yields for the formation of reactive metal radicals.

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Registry No. $[\pi\text{-CpW(CO)}_3]_2$, 12566-66-4; $\pi\text{-CpW(CO)}_3H$, 12128-26-6; $\pi\text{-CpW(CO)}_3I$, 31870-69-6.

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Conjugate Addition of Enolate Anions to Vinylcarbene Complexes

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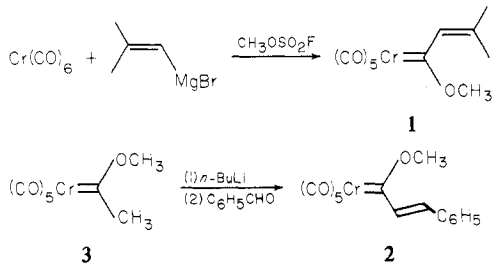
The lithium enolate of cyclopentanone and the potassium enolate of isobutyrophenone conjugately add to (isobutenylmethoxycarbene)pentacarbonylchromium(0), **1**, and to (styrylmethoxycarbene)pentacarbonylchromium(0), **2**, to form new carbene complexes. The lithium enolate of acetone reacted with **1** and **2** to give products derived from addition to the carbene carbon atom. Reaction of the lithium enolate of cyclopentanone with (phenylmethoxycarbene)pentacarbonyltungsten(0), **12**, gave 2-benzylidenecyclopentanone via attack of the enolate carbon on the carbene carbon while the reaction of the potassium enolate of isobutyrophenone and **12** proceeded by attack of the enolate oxygen.

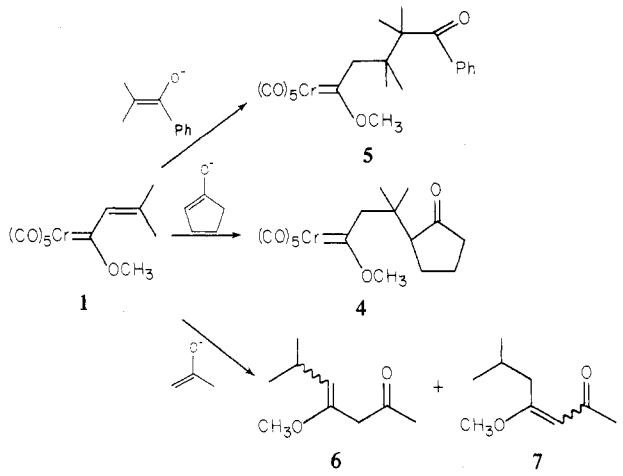
Introduction

The evolution of metal–carbene complexes into useful reagents for organic synthesis[1,2] requires the development of general synthetic methods for the preparation of a wide variety of metal–carbene complexes. Recently, we demonstrated that anions generated α to the carbene carbon of metal–carbene complexes are synthetically useful intermediates for the elaboration of metal–carbene complexes.[3-7] These carbene

Scheme I. Synthesis of Vinylcarbene Complexes



Scheme II



anions are moderately reactive toward reactive electrophiles such as epoxides,[4] α-bromo esters,[4] aldehydes,[3] and chloromethyl methyl ether.[5] Carbene anions are readily generated from metal–carbene complexes using convenient bases such as $NaOCH_3$ or *n*-BuLi.[7-9] Carbene complexes are remarkably acidic; in THF, $(CO)_5CrC(OCH_3)CH_3$ is as acidic as *p*-cyanophenol, which has a pK_a of 8 in water.[9]

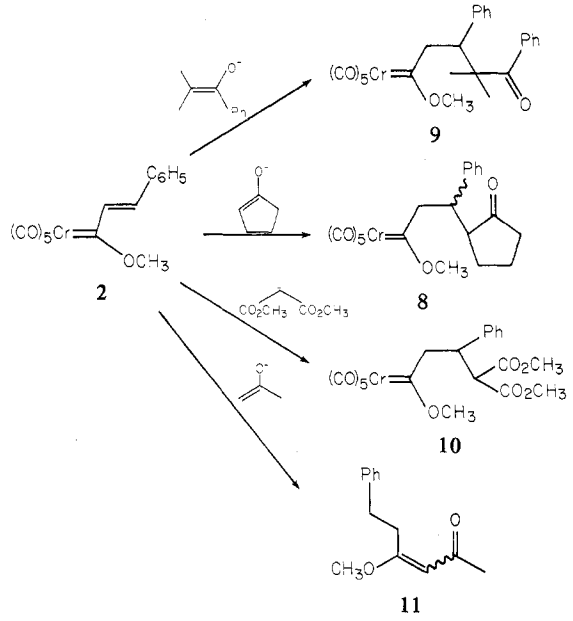
The high thermodynamic stability of carbene anions suggested that their formation might provide the driving force for carbon–carbon bond formation. Consequently, we have studied the addition of nucleophiles to vinylcarbene complexes reasoning that the high stability of carbene anions might make vinylcarbene complexes good Michael acceptors. Earlier we reported the conjugate addition of organolithium and organocopper reagents to vinylcarbene complexes.[10] The conjugate additions of dimethylamine[11] and of diazomethane[12] to an acetylenic carbene complex have been reported. Here we report the conjugate addition of enolate anions to vinylcarbene complexes.

Results

Synthesis of Vinylcarbene Complexes. The two vinylcarbene complexes chosen for study were (isobutenylmethoxycarbene)pentacarbonylchromium(0), **1**, and (styrylmethoxycarbene)pentacarbonylchromium(0), **2**. Compound **2** was prepared in 52% yield by reaction of the carbene anion of $(CO)_5CrC(OCH_3)CH_3$, **3**, with benzaldehyde.[10] Since ketones do not undergo condensation reactions with metal–carbene complexes, **1** could not be prepared from **3** and acetone. Reaction of isobutenylmagnesium bromide with $Cr(CO)_6$ followed by alkylation of the resulting acyl anion with methyl fluorosulfonate gave **1** in 11% yield. (See Scheme I).

Reaction of Enolate Anions with Vinylcarbene Complexes. The reactions of **1** with enolate anions are summarized in Scheme II. The reaction of **1** with the enolate anion of cyclopentanone (generated from the enol acetate and methyllithium at −78 °C) gave a 79% yield of the conjugate addition product **4**. Similarly, the reaction of **1** with the potassium enolate of isobutyrophenone (generated from the ketone and potassium *tert*-butoxide) gave a 71% yield of conjugate addition product **5**. This reaction is remarkable in that carbon–carbon bond formation leads to two adjacent quaternary carbon centers. The reaction of **1** with the sterically less crowded enolate anion of acetone (generated from the corresponding enol acetate and methyllithium) did not give a conjugate addition product. Instead, a 50% yield of a 4:1 mixture of β,γ- and α,β-unsaturated ketones **6** and **7** was obtained. These products probably arise via nucleophilic attack of the enolate carbon atom at the carbene carbon atom. The relative amounts of **6** and **7** were determined by comparison of the NMR integration of the vinyl singlet of **7** at δ 5.4 with that of the vinyl doublet of **6** at δ 4.4. Hydrolysis of both **6** and **7** gave 6-methyl-2,4-heptanedione which was identified by comparison with an authentic sample.

Scheme III

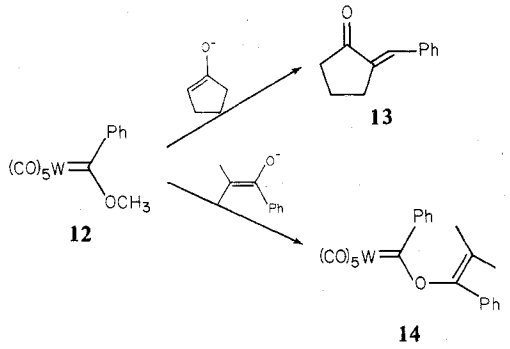


The reactions of styrylcarbene complex **2** with enolate anions closely parallel those of **1** (Scheme III). Reaction of **2** with the lithium enolate of cyclopentanone gave a 79% yield of conjugate addition product **8** as a mixture of diastereomers. Reaction of **2** with the potassium enolate of isobutyrophenone gave a 75% yield of conjugate addition product **9**. Reaction of **2** with the sodium enolate of dimethyl malonate gave a 36% yield of conjugate adduct **10**. Reaction of **2** with the lithium enolate of acetone failed to give a conjugate addition product; a 59% yield of an α,β-unsaturated ketone **11**, presumably resulting from attack of the enolate at the carbene carbon atom, was obtained. The NMR of **11** indicated that only one isomer was present. Hydrolysis of **11** gave 6-phenyl-2,4-hexanedione which was identified by comparison with an authentic sample.

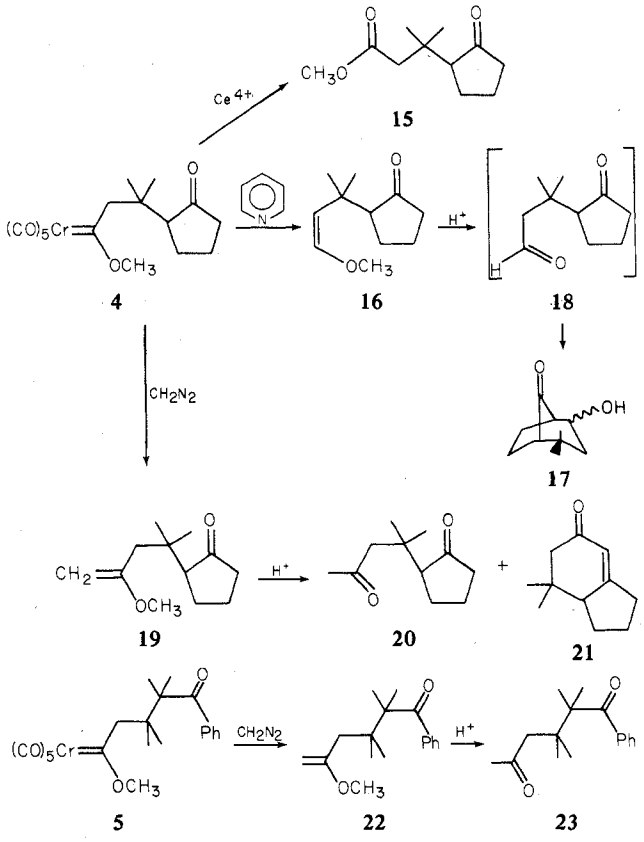
Reaction of Enolate Anions with Arylcarbene Complexes. A brief study was carried out on the reactions of enolates with $(CO)_5WC(OCH_3)C_6H_5$, **12**, which is not subject to 1,4 addition (Scheme IV). Reaction of **12** with the lithium enolate of cyclopentanone gave 2-benzylidenecyclopentanone, **13**, in 46% yield. This product is thought to arise via initial attack of the enolate carbon on the carbene carbon atom. In contrast, the potassium enolate of isobutyrophenone reacts with **12** to give carbene complex **14** via attack of the enolate oxygen at the carbene carbon atom.

Removal of the Carbene Ligand from Conjugate Adducts. A number of synthetically useful ways of removing alkyl-

Scheme IV



Scheme V



alkoxycarbene ligands from their metal complexes have been developed: oxidation leads to esters,[3,13,14] reaction with diazomethane leads to vinyl ethers with an additional carbon atom,[15] and pyridine-catalyzed decomposition leads to vinyl ethers derived from a 1,2 hydrogen shift.[16,17] The synthetic utility of carbene complex **4** was demonstrated by releasing the carbene ligand in three different ways to produce organic products that are the equivalent of adding the enolate of cyclopentanone in a conjugate manner to methyl 3-methyl-2-butenoate, 3-methyl-2-butenal, and mesityl oxide (Scheme V).

Oxidation of **4** with ceric ion gave methyl 3-methyl-3-(2-oxocyclopentyl)butyrate, **15**, in 73% yield. The reaction of **4** with pyridine in heptane for 14 h at 100 °C gave an 82% yield of the (*Z*)-vinyl ether, **16**. The NMR coupling constant of 8 Hz between the vinyl protons of **16** establishes the configuration of the compound as *Z*;[18] none of the *E* isomer was detected. An explanation for the sole formation of the less stable *Z* isomer is presented in the Discussion section. Hydrolysis of vinyl ether **16** with aqueous acid gave a 56% yield of the bicyclic epimeric alcohols **17**. These bicyclic compounds are thought to arise from aldol condensation of an initially formed keto aldehyde **18**.

Reaction of **4** with diazomethane followed by aqueous hydrolysis of the presumed methyl vinyl ether **19** gave a 40% yield of diketone **20** together with a 22% yield of its condensation product, bicyclic enone **21**. An authentic sample of **20** was prepared from 1-trimethylsiloxycyclopentene, mesityl oxide, and $TiCl_4$ using the procedure of Mukaiyama.[19] A sample of bicyclic enone **21** was obtained by base-catalyzed condensation of **20**. The mixture of **20** and **21** derived from **4** was analyzed by gas chromatography and by NMR.

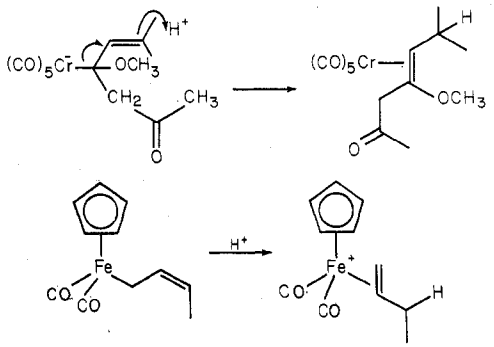
Reaction of conjugate adduct **5** with diazomethane gave a 57% yield of methyl vinyl ether **22**. Hydrolysis of **22** gave a 71% yield of diketone **23**.

Discussion

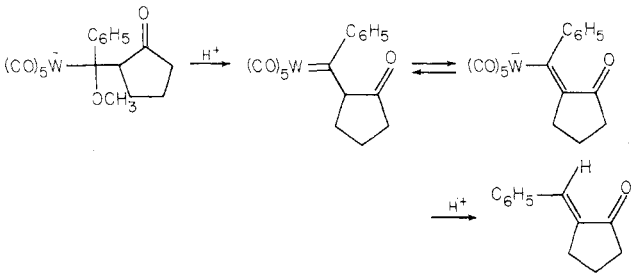
The conjugate addition reactions observed here indicate that the vinylcarbene ligand is an excellent Michael acceptor. This is probably related to the formation of a highly stabilized carbene anion upon conjugate addition to the vinylcarbene unit. It may also be related to the ease of one-electron reduction of vinylcarbene complexes to radical anions. The reduction potential of $(CO)_5CrC(OCH_3)CH{=}C(CH_3)_2$ determined by cyclic voltammetry is −1.8 V;[20] for comparison the reduction potential of $R_2C{=}CHCOCH_3$ is −2.2 V and that of $R_2C{=}CHCO_2CH_3$ is −2.4 V.[21] House has reported a correlation between the reduction potentials of α,β-unsaturated carbonyl compounds and their reactivity toward conjugate addition of organocuprates.[22]

Two sites of reactivity in the vinylcarbene complexes were observed: the remote vinylic carbon atom and the carbene carbon atom. Bulky nucleophiles such as the enolates of cyclopentanone, isobutyrophenone, or dimethyl malonate attacked only at the sterically more accessible remote vinylic position. These conjugate addition reactions might proceed either via direct nucleophilic attack of the enolate anion at the vinylic carbon atom or via initial electron transfer from the enolate to the vinylcarbene complex followed by coupling of the radical anion of the carbene complex with the α-keto radical.

The reaction of vinylcarbene complexes with the less bulky enolate anion of acetone apparently proceeds via nucleophilic attack at the carbene carbon atom. The initial adduct is a σ-allylchromium anion which can react with acid at the remote allylic position to produce the observed vinyl ether products. Electrophilic attack at the remote vinylic carbon atom is well-known for σ-allyliron compounds.[23]



The enolate of cyclopentanone can attack the carbene carbon atom of $(CO)_5WC(OCH_3)C_6H_5$, **12**, in which there is no site available for conjugate addition. 2-Benzylidenecyclopentanone, **13**, probably arises via acid-catalyzed conversion of the initial adduct to a metal–carbene complex which then undergoes decomposition via a 1,2 proton shift.

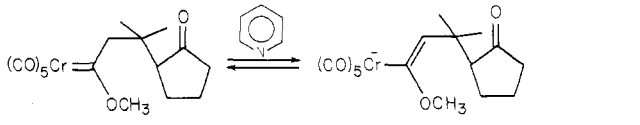


13

Our synthesis of $(CO)_5WC(C_6H_5)_2$ involved the acid-catalyzed loss of methoxide from a similar adduct, $(CO)_5WC(OCH_3)(C_6H_5)_2^-$.[24] Decomposition of alkylcarbene complexes via a net 1,2 proton shift has been observed previously in the decomposition of $(CO)_5CrC(CH_2)_3O$ to dihydrofuran[17] and of $(CO)_5WC(C_6H_5)CH_3$ to $(CO)_5W(CH_2{=}CHC_6H_5)$.[25,26] The 1,2 proton shift probably occurs by reversible deprotonation to give an anion stabilized by the ketone and carbene functionalities[9] followed by protonation of the carbon–metal bond of the intermediate anion.

The enolate of isobutyrophenone is so sterically crowded that reaction with **12** occurs only via the less hindered oxygen atom of the enolate to give carbene complex **14**. Thus, although nucleophilic attack at the remote site of a vinylcarbene complex is so insensitive to steric effects that a new bond can be formed to give two adjacent quaternary centers, nucleophilic attack at the carbene carbon atom is very sensitive to the size of the entering nucleophile.

The highly stereoselective formation of the less stable (*Z*)-vinyl ether **16** in the pyridine-catalyzed decomposition of carbene complex **4** is interesting and potentially synthetically useful. The 1,2 proton shift observed in this reaction has been shown to proceed by a pathway not involving a free carbene.[9] The reaction probably proceeds by a mechanism similar to that proposed above for the formation of **13**. The high acidity of protons α to the carbene carbon atom in metal–carbene complexes could lead to reversible deprotonation of **4** by pyridine. The favored carbene anion would be expected to have the large $Cr(CO)_5$ and tertiary alkyl groups trans to one another. Protonation of the carbon–metal bond of this anion leads directly to **16**.



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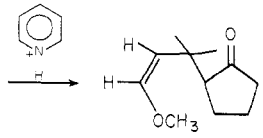
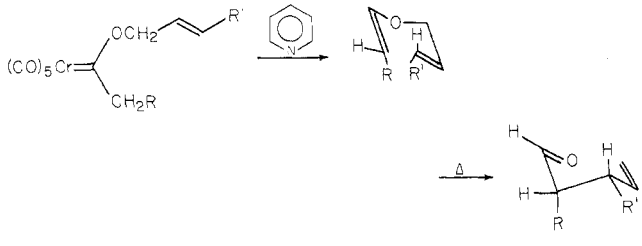
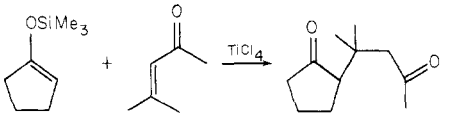


16

It should be possible to prepare isomerically pure allyl vinyl ethers by this route and to use the sterochemistry of the *Z*-vinyl ether in a Claisen rearrangement[27] to stereospecifically generate a new asymmetric center.



The conjugate addition reactions of vinylcarbene complexes and enolate anions are useful in preparing new carbene complexes possessing ketone and ester functionalities. Such functionalized carbene complexes cannot be prepared by the usual routes involving reaction of organolithium reagents with metal carbonyls. Since the functionalized carbene complexes prepared by conjugate addition reactions can be cleaved to form esters, aldehydes, and ketones, the net transformations described here are the synthetic equivalent of Michael additions of enolates to α,β-unsaturated carbonyl compounds. The steric insensitivity of the conjugate addition of enolates to vinylcarbene complexes should be useful synthetically. The addition of the enolate of isobutyrophenone to **1** generates two adjacent quaternary centers and has not been accomplished with α,β-unsaturated carbonyl compounds. Michael additions to β,β-disubstituted α,β-unsaturated carbonyl compounds are difficult to accomplish. For example, there are no known examples of a Michael addition of cyclopentanone to a β-monosubstituted or β,β-disubstituted α,β-unsaturated ester. Cyclopentanone undergoes self-condensation[28] rather than adding to 2-methyl-1-buten-3-one which should be susceptible to conjugate addition since it possesses no β substituents. Recently, Mukaiyama has observed the $TiCl_4$-catalyzed addition of 1-trimethylsiloxycyclopentene to mesityl oxide which circumvents many of the problems of Michael additions to β,β-disubstituted α,β-unsaturated carbonyl compounds.[19] Our conjugate additions to vinylcarbene complexes involve fundamentally different reaction conditions and should complement Mukaiyama's procedure.



Experimental Section

General Information. All reactions were carried out in flame-dried flasks under a nitrogen atmosphere. Ether and tetrahydrofuran (THF) were distilled from sodium and benzophenone under a nitrogen atmosphere. NMR spectra were taken using a JEOLCO MH-100 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 267 infrared spectrometer or on a Beckman IR-8 spectrophotometer. Mass spectra were taken using a AEI-902 mass spectrometer at 70 eV or a Varian CH-7 GC mass spectrometer. For carbene complexes, the intensities of peaks from successive loss of CO ligands are listed in addition to all peaks with greater than 10% relative intensity. Gas chromatographic analyses were performed using a Hewlett-Packard Model 5750 research chromatograph. Preparative thin-layer chromatography (TLC) was performed on Merck PF-254 silica gel. UV–VIS spectra were recorded on a Cary 15 UV–VIS spectrophotometer. A Thomas-Hoover capillary melting point apparatus was used to determine melting points which are uncorrected.

(Isobutenylmethoxycarbene)pentacarbonylchromium(0), 1. Isobutenylmagnesium bromide was prepared by heating isobutenyl bromide (6.8 g, 0.05 mol) and Mg (1.22 g, 0.05 mol) in 20 ml of dry THF. The resulting brown mixture was diluted with 30 ml of THF, transferred to a flask containing $Cr(CO)_6$ (4 g, 18.2 mmol), and stirred 4.5 h at 25 °C. Solvent was removed under vacuum and $MeOSO_2F$ (1.5 ml, 18.5 mmol) was added. The residue was dissolved in 50 ml of Et_2O and washed twice with 50 ml of H_2O and dried (Na_2SO_4). Column chromatography (hexane) afforded **1** (0.56 g, 11%) as a bright red solid: mp 35–37 °C; NMR (CS_2) δ 1.87 (s, 3 H, CH_3), 1.90 (s, 3 H, CH_3), 4.72 (s, 3 H, OCH_3), 7.27 (br s, 1 H, CH=C); IR (hexane) ν_{CO} 2064 (w), 1986 (w), 1961 (m), 1949 (s) cm^{-1}; exact mass 289.9890 (calcd for $C_{11}H_{10}O_6Cr$ 289.9881); MS (*m/e*, %) 290 (14) M^+, 262 (7) M – 1CO, 234 (4) M – 2CO, 206 (9) M – 3CO, 178 (19) M – 4CO, 150 (69) M – 5CO, 120 (20), 107 (14), 98 (19), 91 (11), 83 (31), 82 (15), 80 (15), 67 (15), 55 (26), 53 (15), 52 (100).

Reaction of 1 with the Lithium Enolate of Cyclopentanone. The lithium enolate of cyclopentanone was prepared by the method of House.[29] MeLi (0.56 ml, 1.14 M, 0.64 mmol) and 1-acetoxycyclopentene (49 mg, 0.39 mmol) were combined in 10 ml of THF at –78 °C and the solution was stirred 15 min. The solution was

transferred into 5 ml of THF at −78 °C containing **1** (100 mg, 0.345 mmol). Within minutes the color became light orange and after 1 h of stirring, HCl–Et_2O (0.25 ml, 2.8 M, 0.70 mmol) was injected at −78 °C and the solution warmed to 25 °C. Preparative TLC (2:1 hexane–Et_2O) gave **1** (9 mg, 9%, R_f 0.42) and **4** (93 mg, 79%, R_f 0.21) as a yellow solid: mp 52–54 °C; NMR ($CDCl_3$) δ 0.96 (s, 3 H, diastereotopic CH_3), 1.00 (s, 3 H, diastereotopic CH_3), 1.6–2.3 (mult, 7 H), 3.64 (s, 2 H, $CH_2C{=}Cr$), 4.72 (s, 3 H, OCH_3); IR (hexane) ν_{CO} 2064 (w), 1991 (m), 1963 (s) cm^{-1}, C=O of ketone at 1741 cm^{-1}; exact mass on M − 5CO peak 234.0704 (calcd for $C_{11}H_{18}O_2Cr$ 234.0711); MS (*m/e*, %) 374 (<1) M^+, 346 (<1) M − 1CO, 318 (<1) M − 2CO, 290 (<1) M − 3CO, 262 (<1) M − 4CO, 234 (1) M − 5CO, 168 (12), 167 (100), 166 (18), 151 (51), 149 (14), 138 (19), 136 (12), 135 (24), 123 (36), 119 (14), 109 (13), 108 (19), 107 (43), 105 (13), 99 (15), 95 (19), 93 (23), 83 (19), 82 (99), 79 (41), 77 (41), 67 (45), 64 (20), 55 (36), 53 (27), 52 (8).

Reaction of 1 with the Potassium Enolate of Isobutyrophenone. The potassium enolate of isobutyrophenone was prepared by the addition of KO-*t*-Bu (39 mg, 0.345 mmol) to isobutyrophenone (51 mg, 0.345 mmol) in 5 ml of THF at 0 °C. After 15 min, the enolate solution was added to **1** (100 mg, 0.345 mmol) in 5 ml of THF at −78 °C to give an orange color after the last of the enolate was added. After 40 min, HCl in Et_2O (0.14 ml, 2.5 M, 0.35 mmol) was injected into the −78 °C solution. Preparative TLC (3:1 hexane–Et_2O) yielded **1** (20 mg, 20%, R_f 0.65) and **5** (87 mg, 71%, based on recovered **1**, R_f 0.50) as a yellow solid: mp 82–85 °C; NMR ($CDCl_3$) δ 1.12 (s, 6 H, 2 CH_3's), 1.30 (s, 6 H, 2 CH_3's), 3.70 (s, 2 H, CH_2) 4.80 (s, 3 H, OCH_3), 7.42 (s, 5 H, C_6H_5); IR (hexane) ν_{CO} 2063 (w), 1984 (w), 1961 (m), 1946 (s) cm^{-1}; exact mass of M − 2CO peak 382.0881 (calcd for $C_{19}H_{22}O_5Cr$ 382.0871); MS (*m/e*, %) 298 (3) M − 5CO, 246 (24), 231 (10), 220 (47), 215 (33), 172 (16), 157 (50), 131 (36), 130 (93), 118 (14), 115 (21), 108 (57), 105 (81), 99 (16), 91 (32), 84 (32), 83 (36), 80 (93), 77 (22), 52 (100).

Anal. Calcd for $C_{21}H_{22}O_7Cr$: C, 57.52; H, 5.06; Cr, 11.86. Found: C, 57.65; H, 5.10; Cr, 11.39.

Reaction of 1 with the Lithium Enolate of Acetone. MeLi (1.06 ml, 1.14 M, 1.21 mmol) was added to isopropenyl acetate (72 mg, 0.72 mmol, Aldrich) in 5 ml of THF at −78 °C. After 30 min at −78 °C, the enolate solution was added to **1** (200 mg, 0.69 mmol) in 5 ml of THF at −78 °C and the solution stirred for 1 h. HCl–Et_2O (0.50 ml, 2.8 M, 1.40 mmol) was added to the orange solution at −78 °C to give a brown-orange color. Preparative TLC (1:1 hexane–Et_2O) gave an orange band for **1** (R_f 0.57, 5 mg, 2%) and a wide colorless band which yielded a colorless oil (R_f 0.28, 51 mg, 50%) that was identified as a 1:4 mixture of the α,β- and β,γ-unsaturated ketones **6** and **7** according to NMR: NMR of **6** ($CDCl_3$) δ 4.4 (d, J = 9 Hz, 1 H, C=CH), 3.5 (s, 3 H, OCH_3), 3.12 (s, 2 H, $-CH_2CO-$), 2.6 (m 1 H), 2.18 (s, 3 H, CH_3CO), 0.93 (d, J = 7 Hz, 6 H, $-CH(CH_3)_2$); NMR of **7** ($CDCl_3$) δ 5.42 (s, 1 H, C=CH), 3.6 (s, 3 H, OCH_3), 2.6 (d, J = 7 Hz, 2 H, $CH_2C{=}C$), 2.16 (s, 3 H, CH_3CO), 1.9 (m, 1 H), 0.88 (d, J = 6 Hz, 6 H, $CH(CH_3)_2$).

Hydrolysis of the mixture of **6** and **7** with 1 ml of 3 N HCl and 2 ml of Et_2O overnight afforded the enol of 6-methyl-2,4-heptanedione whose IR and NMR spectra were superimposable upon those of an authentic sample prepared from the dianion of 2,4-pentanedione and isopropyl bromide: NMR (CCl_4) δ 0.91 (mult, 6 H, CH_3), 1.9–2.2 (mult, 6 H, $CH_3C{=}O$ and $CHCH_2$), 5.30 (s, 1 H, HC=C), 15.4 (br s, 1 H, OH); IR (film) 2960 (s), 2927 (s), 2872 (s), 1705 (m), 1600 (s), 1460 (m), 1364 (m) cm^{-1}.

Reaction of 2 with the Lithium Enolate of Cyclopentanone. The lithium enolate of cyclopentanone was prepared from 1-acetoxycyclopentene (43 mg, 0.34 mmol) and MeLi (0.56 ml, 1.14 M, 0.64 mmol active base) at −78 °C in 5 ml of THF. After 15 min, the enolate solution was added to **2**[10] (110 mg, 0.326 mmol) in 5 ml of THF at −78 °C. After 50 min at −78 °C, the solution changed color from deep red to light red. HCL–Et_2O (0.25 ml, 2.8 M, 0.70 mmol) was injected at −78 °C and the color remained light red. Solvent was removed and preparative TLC (hexane) gave **2** (7 mg, 6%, R_f 0.38) and a yellow band that yielded **8** (102 mg, 79%, R_f 0.17) as a yellow oil: NMR ($CDCl_3$) δ 1.3–2.4 (mult, 7 H), 3.4–4.2 (mult, 3 H, $CHCH_2C{=}Cr$), 4.65 (s, 3 H, OCH_3), 7.0–7.4 (mult, 5 H, C_6H_5); IR (hexane) ν_{CO} 2065 (w), 1991 (w), 1962 (s, sh), 1952 (s) cm^{-1}, C=O of ketone at 1747 cm^{-1}; exact mass 422.0476 (calcd for $C_{20}H_{18}O_7Cr$ 422.0476).

Reaction of 2 with the Potassium Enolate of Isobutyrophenone. Isobutyrophenone (43 mg, 0.29 mmol) and potassium *tert*-butoxide (30 mg, 0.29 mmol) were combined in 5 ml of THF and stirred 15 min at 0 °C. The solution was then added to **2**[10] (90 mg, 0.266 mmol) in 5 ml of THF at −78 °C. After 40 min at −78 °C, HCl in ether (0.13 ml, 2.5 M, 0.325 mmol) was injected into the light red solution but with no color change. Preparative TLC (2:1 hexane–Et_2O) gave a red band (R_f 0.41) that consisted of a 1:1 mixture of **2** (11 mg, 12%) and isobutyrophenone (10 mg, 23%) according to NMR. A yellow band (R_f 0.27) afforded 85 mg (75% based on recovered **2**) of **9** as a yellow oil: NMR ($CDCl_3$) δ 1.15 (s, 3 H, diastereotopic CH_3), 1.30 (s, 3 H, diastereotopic CH_3), 3.50 (dd, J = 4, 17 Hz, 1 H of diastereotopic CH_2), 3.94 (dd, J = 4, 10 Hz, 1 H, CH), 4.38 (dd, J = 10, 17 Hz, 1 H of diastereotopic CH_2), 4.41 (s, 3 H, OCH_3), 7.1–7.5 (mult, 10 H, C_6H_5); IR (hexane) ν_{CO} 2065 (w), 1983 (w), 1948 (s) cm^{-1}; exact mass 486.0762 (calcd for $C_{25}H_{22}O_7Cr$ 486.0769); MS (*m/e*, %) 486 (<1) M^+, 458 (<1) M − 1CO, 430 (<1) M − 2CO, 402 (<1) M − 3CO, 374 (<1) M − 4CO, 346 (2) M − 5CO, 294 (10), 263 (15), 220 (27), 205 (15), 162 (44), 161 (13), 147 (12), 132 (40), 131 (100), 121 (14), 117 (17), 115 (19), 108 (44), 105 (46), 103 (50), 91 (46), 86 (50), 84 (76), 80 (77), 77 (55), 52 (93).

Reaction of 2 with Sodium Dimethyl Malonate. Sodium dimethyl malonate (55 mg, 0.357 mmol) was added to **2**[10] (100 mg, 0.296 mmol) in 10 ml of THF at 0 °C. The deep red color became light and after 30 min HCl in Et_2O (0.10 ml, 2.82 M, 0.282 mmol) was injected and solvent was removed. Preparative TLC (hexane) afforded **2** (7 mg, 7%, R_f ~0.4) and **10** (46 mg, 36%, R_f 0.20) as an orange oil: NMR ($CDCl_3$) δ 3.44 (s, 3 H, diastereotopic CO_2Me), 3.5–4.2 (mult, 4 H, CH_2CHCH), 3.78 (s, 3 H, diastereotopic CO_2Me), 4.65 (s, 3 H, OCH_3), 7.20 (mult, 5 H, C_6H_5); IR (hexane) ν_{CO} 2064 (w), 1988 (w), 1961 (s, sh), 1949 (s) cm^{-1}, C=O of ester at 1745 cm^{-1}; exact mass 470.0292 (calcd for $C_{20}H_{18}O_{10}Cr$ 470.0303); MS (*m/e*, %) 470 (<1) M^+, 442 (<1) M − 1CO, 414 (<1) M − 2CO, 386 (1) M − 3CO, 358 (2) M − 4CO, 330 (2) M − 5CO, 234 (21), 231 (11), 203 (13), 202 (22), 189 (12), 176 (13), 175 (100), 174 (33), 171 (11), 147 (15), 131 (46), 121 (58), 115 (41), 104 (24), 103 (37), 102 (11), 101 (13), 91 (24), 78 (14), 77 (27), 64 (25), 59 (34).

Reaction of 2 with the Lithium Enolate of Acetone. The lithium enolate of acetone was prepared by the addition of MeLi (0.50 ml, 1.14 M active base, 0.57 mmol) to isopropenyl acetate (30 mg, 0.30 mmol) in 5 ml of THF at −78 °C. The solution was stirred 20 min at −78 °C and then added to **2** (100 mg, 0.296 mmol) in 5 ml of THF at −78 °C. The dark red solution became orange after stirring for 30 min at −78 °C. HCl–Et_2O (0.25 ml, 2.8 M, 0.70 mmol) was injected at −78 °C and the solution was warmed to 25 °C. Preparative TLC (3:1 Et_2O–hexane) yielded the enone **11** (38 mg, 59%, R_f 0.31) as a colorless oil: NMR ($CDCl_3$) δ 2.14 (s, 3 H, $CH_3C{=}O$), 2.7–3.2 (mult, 4 H, CH_2CH_2), 3.58 (s, 3 H, OCH_3), 5.41 (s, 1 H, CH=C), 7.20 (s, 5 H, C_6H_5); IR (CCl_4) 1682 (s) cm^{-1} (conjugated C=O).

Hydrolysis of **11** with 0.5 ml of 3 N HCl and 2 ml of Et_2O for 24 h at 25 °C gave 6-phenyl-2,4-hexanedione which was identified by spectral comparison with an authentic sample prepared by the procedure of Hauser.[30]

Reaction of 12 with the Lithium Enolate of Cyclopentanone. The lithium enolate of cyclopentanone was generated as before from MeLi (0.56 ml, 0.64 mmol) and 1-acetoxycyclopentene (43 mg, 0.34 mmol) in THF at −78 °C. The enolate solution was added to **12** (145 mg, 0.326 mmol) in 5 ml of THF at −78 °C and after 40 min at −78 °C the color had changed from light red to orange. Upon addition of HCl in Et_2O (0.25 ml, 2.8 M, 0.70 mmol) at −78 °C the solution turned dark brown. Solvent was removed and preparative TLC (2:1 hexane–Et_2O) gave 2-benzylidenecyclopentanone, **13** (26 mg, 46%, R_f 0.22), as a pale yellow solid, mp 65–68 °C (lit.[31] mp 71 °C), which was identified by comparison of its NMR and IR spectra with those of an authentic sample: NMR ($CDCl_3$) δ 2.0–2.8 (mult, 4 H, CH_2CH_2), 3.00 (d of t, J = 3, 7 Hz, 2 H, $CH_2C{=}C$), 7.3–7.8 (mult, 6 H, CH=C and C_6H_5); IR (CCl_4) 1720 (s), 1629 (s), 1454 (m), 1177 (s), 694 (m) cm^{-1}.

Reaction of 12 with the Potassium Enolate of Isobutyrophenone. The enolate was obtained by the addition of potassium *tert*-butoxide (75 mg, 0.67 mmol) to isobutyrophenone (99 mg, 0.67 mmol) in 5 ml of THF at −78 °C. The solution was stirred 20 min and then added to **12** (222 mg, 0.50 mmol) in 5 ml of THF at −78 °C. After 15 min of stirring at −78 °C, HCl in ether (0.28 ml, 2.5 M, 0.70 mmol) was injected at −78 °C to give a dark red color. Solvent was removed and preparative TLC (hexane) gave a red-orange band (R_f 0.33, 32 mg, 15% recovery) for **12** and a red-brown band (R_f 0.45, 101 mg) which consisted of a 3:1 mixture of **14** (36%) to **12** (12%) according

to NMR. Compound **14** was obtained pure by reapplying the mixture to preparative TLC and extracting with ether the top half of the band to give a deep red solid: mp 103–106 °C; NMR ($CDCl_3$) δ 1.83 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3), 7.27–7.65 (mult, 10 H, C_6H_5); IR (hexane) ν_{CO} 2073 (w), 1992 (w), 1962 (s), 1933 (s) cm^{-1}; exact mass 560.0451 (calcd for $C_{22}H_{16}O_6W$ 560.0456); MS (*m/e*, %) 560 (<1) M^+, 532 (<1) M – 1CO, 504 (<1) M – 2CO, 476 (<1) M – 3CO, 448 (2) M – 4CO, 420 (2) M – 5CO, 261 (5), 252 (5), 136 (6), 131 (5), 122 (31), 115 (5), 106 (12), 105 (100), 91 (13), 86 (25), 84 (37), 77 (57), 51 (23).

Oxidation of 4 with Ceric Ammonium Nitrate. Ceric ammonium nitrate (0.37 g, 0.678 mmol) was added to **4** (84.5 mg, 0.226 mmol) in 10 ml of reagent grade acetone at 25 °C. After 5 min of stirring, the resulting green solution was concentrated and preparative TLC (2:1 Et_2O–hexane) gave methyl 3-(2-oxocyclopentyl)-3-methylbutyrate, **15** (32.6 mg, 73%, R_f 0.50), as a colorless oil: NMR ($CDCl_3$) δ 1.06 (br s, 6 H, diastereotopic CH_3), 1.6–2.4 (br mult, 7 H of cyclopentanone), 2.36 (d, J = 14 Hz, 1 H of diastereotopic CH_2CO_2Me), 2.65 (d, J = 14 Hz, 1 H of diastereomeric CH_2CO_2Me), 3.64 (s, 3 H, OCH_3); IR (neat) 2970 (s), 2880 (m), 1730 (s), 1434 (m), 1369 (m), 1330 (m), 1231 (m), 1148 (m), 1020 (m) cm^{-1}; exact mass 198.1252 (calcd for $C_{11}H_{18}O_3$ 198.1255); MS (*m/e*, %) 198 (11), 167 (20), 166 (31), 151 (47), 125 (100), 124 (28), 115 (21), 97 (14), 84 (70), 83 (78), 82 (15), 81 (15), 73 (28), 69 (22), 55 (65).

Pyridine-Catalyzed Decomposition of 4. A solution of **4** (103 mg, 0.28 mmol) and pyridine (260 μl, 3.36 mmol) in 10 ml of degassed heptane was heated to 100 °C for 14 h. Preparative TLC (1:1 Et_2O–hexane) of the concentrated solution gave (*Z*)-1-methoxy-3-methyl-3-(2-oxocyclopentyl)-1-butene, **16** (41 mg, 82%, R_f 0.27), as a colorless oil: NMR ($CDCl_3$) δ 1.17 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.5–2.4 (mult, 7 H of cyclopentanone), 3.53 (s, 3 H, OCH_3), 4.24 (d, J = 8 Hz, C=CH), 5.72 (d, J = 8 Hz, C=CH); IR (neat) 2960 (s), 2875 (m), 1730 (s), 1655 (s), 1460 (m), 1273 (m), 1156 (m), 1100 (s) cm^{-1}. The 8-Hz coupling of the vinyl hydrogens establishes the *Z* configuration of **16**. For the isomeric β-methoxystyrenes, the coupling between the vinyl hydrogens is 7.1 Hz in the *Z* isomer and 13.0 Hz in the *E* isomer.[18]

Hydrolysis of vinyl ether **16** with 2 N HCl gave a mixture of epimers of 4,4-dimethylbicyclo[3.2.1]octan-2-ol-8-one, **17** (21 mg, 56%): NMR ($CDCl_3$) δ 0.90, 0.94, 0.97, 1.15 (singlets, 6 H, 4 CH_3 peaks), 1.4–2.0 (br mult, 7 H, 3 CH_2's and 1 bridgehead H or OH), 2.30 (br s, 1 H, OH or bridgehead H), 2.70 (mult, 1 H, OH or bridgehead H), 3.95–4.15 (mult, 1 H, CHO); IR (film) 3420 (s) OH, 2960 (s), 2880 (s), 1740 (s) C=O, 1371 (m), 1180 (m), 1159 (m), 1049 (m), 1030 (m), 999 (w) cm^{-1}; exact mass 168.1153 (calcd for $C_{10}H_{16}O_2$) 168.1150.

Reaction of 4 with Diazomethane. Diazomethane was prepared from *N*-methyl-*N*-nitrosourea (1.1 g, 10.6 mmol) and 4 ml of 40% KOH in 6 ml of benzene at 5–10 °C.[32] After drying over K_2CO_3, the benzene solution was added to **4** (78 mg, 0.21 mmol) and the solution was stirred at 10–25 °C for 30 min. Preparative TLC (1:1 hexane–ether) gave a colorless band (R_f 0.45) which yielded 24 mg of a 2:1 mixture of the diketone **20** (43%) and the bicyclic enone **21** (22% as determined by NMR and gas chromatographic comparison) (6-ft, 10% OV 225, 170 °C) with authentic samples.

Following the procedure of Mukaiyama,[19] reaction of 1-trimethylsiloxycyclopentene[33] with mesityl oxide and $TiCl_4$ in CH_2Cl_2 at −78 °C gave a 37% yield of diketone **20**: NMR ($CDCl_3$) δ 1.00 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 1.5–2.2 (mult, 7 H of cyclopentanone ring), 2.10 (s, 3 H, CH_3C=O), 2.42 (d, J = 16 Hz, 1 H of CH_2C=O), 2.94 (d, J = 16 Hz, 1 H of CH_2C=O); IR (neat) 2967 (s), 2878 (m), 1736 (s), 1411 (m), 1369 (m), 1150 (m) cm^{-1}.

Diketone **20** (100 mg, 0.55 mmol) was dissolved in 3 ml of ether, and 3 ml of 2 N NaOH was added. After 6 h at room temperature, the ether layer was separated and dried ($MgSO_4$). Preparative TLC (1:1 hexane–ether) gave bicyclic enone **21** (49 mg, 51%, R_f 0.33, mp 65–67 °C); NMR ($CDCl_3$) δ 0.83 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.2–2.0 (mult, 4 H, CH_2CH_2), 2.19 (s, 2 H, CH_2C=O), 2.3–2.5 (mult, 3 H, CH_2C=C and HCC=C), 5.81 (mult, 1 H, HC=C); IR (CCl_4) 2980 (m), 2886 (w), 1668 (s), 1377 (m), 1355 (m), 1280 (m), 1118 (m) cm^{-1}; exact mass 164.1200 (calcd for $C_{11}H_{16}O$ 164.1201); MS (*m/e*, %) 165 (10), 164 (75), 122 (30), 121 (14), 109 (31), 108 (100), 93 (12), 91 (11), 81 (12), 80 (39), 79 (37), 77 (21), 67 (11), 55 (12), 53 (14).

Reaction of 5 with Diazomethane. Diazomethane was prepared from *N*-methyl-*N*-nitrosourea (1.1 g, 10.6 mmol) and 2 ml of 40% KOH in 3 ml of benzene at 5–10 °C.[32] The yellow benzene solution was added to **5** (79 mg, 0.18 mmol) and stirred for 1 h at 10 °C and 1 h at 25 °C. Preparative TLC (2:1 hexane–Et_2O) after two elutions afforded **5** (R_f 0.45, 19 mg, 24% recovery) and 5-methoxy-1-phenyl-2,2,3,3-tetramethyl-5-hexen-1-one, **22** (20 mg, 57% based on recovered **5**, R_f 0.55), as a colorless oil: NMR ($CDCl_3$) δ 1.03 (s, 6 H, 2 CH_3's), 1.27 (s, 6 H, 2 CH_3's), 2.25 (s, 2 H, CH_2), 3.46 (s, 3 H, OCH_3), 3.86 (d, J = 2 Hz, C=CH), 3.97 (d, J = 2 Hz, C=CH), 7.38 (mult, 5 H, C_6H_5); IR (neat) 2979 (s), 1666 (s) conjugated C=O, 1470 (s), 1327 (7), 1260 (s), 1061 (s), 960 (s), 800 (m), 700 (s) cm^{-1}.

Acid-catalyzed hydrolysis of **22** (27 mg, 0.104 mmol) in ether overnight with 0.5 ml of 2 N HCl gave 1-phenyl-2,2,3,3-tetramethyl-1,5-hexanedione (18 mg, 71%, R_f 0.50) which was isolated by preparative TLC. NMR ($CDCl_3$) δ 1.16 (s, 6 H, 2 CH_3's), 1.28 (s, 6 H, 2 CH_3's), 2.13 (s, 3 H, CH_3C=O), 2.65 (s, 2 H, CH_2C=O), 7.36 (mult, 5 H, C_6H_5); IR (neat) 2980 (s), 1710 (s) C=O, 1666 (s) conjugated C=O, 1470 (m), 1358 (m), 1254 (m), 962 (m), 700 (m) cm^{-1}; exact mass 246.1622 (calcd for $C_{16}H_{22}O_2$ 246.1619); MS (*m/e*, %) 148 (42), 141 (27), 123 (10), 105 (100), 85 (6), 84 (75), 83 (50), 57 (6), 55 (15), 51 (12).

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Registry No. **1**, 60920-65-2; **2**, 54873-11-9; **4**, 60920-66-3; **5**, 60920-67-4; **6**, 60909-19-5; **7**, 18369-34-1; **8**, 60920-68-5; **9**, 60920-69-6; **10**, 60920-70-9; **11**, 60909-20-8; **12**, 37823-96-4; **13**, 5679-13-0; **14**, 60920-71-0; **15**, 60909-21-9; **16**, 60909-22-0; **17**, 60909-23-1; **20**, 53857-08-2; **21**, 60934-66-9; **22**, 60909-24-2; **23**, 60909-25-3; isobutenyl bromide, 3017-69-4; $Cr(CO)_6$, 13007-92-6; $MeOSO_2F$, 421-20-5; MeLi, 917-54-4; 1-acetoxycyclopentene, 933-06-2; KO-*t*-Bu, 865-47-4; isobutyrophenone, 611-70-1; isopropenyl acetate, 591-87-7; sodium dimethyl malonate, 18424-76-5; ceric ammonium nitrate, 16593-75-2; *N*-methyl-*N*-nitrosourea, 684-93-5.

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