Coupling of Cyclobutenediones with Fischer Carbene Complexes: A One-Step Synthesis of Cyclopentenediones and/or 5-Alkylidenefuranones via Net Insertion of the Carbene Unit into a C−C Bond[1]

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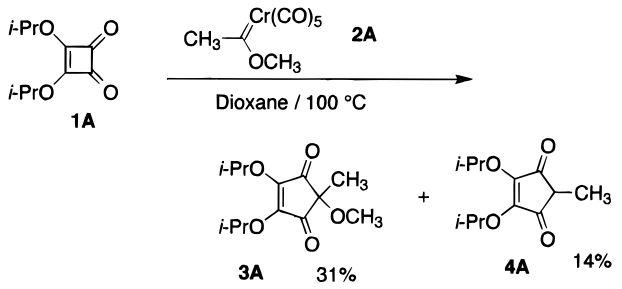
The reaction of Fischer carbene−chromium complexes with 3-cyclobutene-1,2-diones has been investigated. In most cases, the major product of the reaction is the C−C bond insertion product, a 2-alkoxy-4-cyclopentene-1,3-dione, accompanied by a minor amount of the partial deoxygenation product, a 4-cyclopentene-1,3-dione. In some cases, 5-alkylidenefuranones are also formed. A mechanism involving oxidative addition of the coordinatively unsaturated Fischer carbene complex followed by acyl migration and reductive elimination was proposed to account for cyclopentenedione formation. Furanone formation was thought to arise via demetalation of the acyl migration product, followed by O-acylation. An electronic dependence was noted for cyclopentenedione/alkylidene−furanone ratio, which was evaluated using the Hammett equation.

Introduction

Fischer carbene complexes have emerged as powerful tools in organic synthesis.[4] An early and continuing aspect of these studies has been the use of Fischer carbene complexes as substitutes for simple carbenes or carbenoids in classical reaction processes of these reactive intermediates. Many examples utilizing Fischer carbene complexes in the most notable carbene reaction, cyclopropanation of alkenes, have been reported.[5] Imitations of other simple carbene reactions, including C−H insertion,[6] other element−H insertion,[7] and Wagner−Meerwein-type shifts,[8] have also been demonstrated. Lesser known are C−C bond insertion processes.[1,9] In a recent study, the coupling of cyclobutenediones and Fischer carbene complexes was reported.[1] The reaction produces cyclopentenediones (e.g., **3** and **4**, Scheme 1), which are the product of a net insertion of the carbene unit into the acyl−acyl bond of the cyclobutenedione. This article constitutes a more detailed study of the coupling of cyclobutenediones with Fischer carbene complexes.

Scheme 1



Results

Coupling of Alkylcarbene Complexes with Cyclobutenediones. The reaction of a variety of cyclobutenediones with a variety of Fischer carbene complexes is presented in Table 1. The reaction of alkylcarbene complexes with cyclobutenediones produced a mixture of cyclopentenedione **3** and a lesser amount of monodeoxygenated[10] cyclopentenedione **4** (entries A−C, E, and K). Aminocarbene complex **2B** (entry B) was somewhat unreactive and afforded adduct

(1) For a preliminary account of this work, see: Zora, M.; Herndon, J. W. *Organometallics* **1993**, *12*, 248−249.

(2) (a) Middle East Technical University. (b) University of Maryland. (c) New Mexico State University.

(3) Address all correspondence to this author at New Mexico State University.

(4) Numerous reviews of the use of Fischer carbene complexes in organic synthesis have appeared; the most recent include: (a) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187−198. (b) Wulff, W. D. *Organometallics* **1998**, *17*, 3116−3134. (c) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271−288. (d) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163−242. (e) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105−4128.

(5) For the most recent paper focusing on Fischer carbene cyclopropanations, see: Barluenga, J.; Fernandez-Acebes, A.; Trabanco, A. A.; Florez, J. *J. Am. Chem. Soc.* **1997**, *119*, 7591−7592.

(6) See: Sierra, M. A.; Macheño, M. J.; Sáez, E.; del Amo, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 6812−6813, and references therein.

(7) For recent examples, see: (a) Mak, C. C.; Tse, M. K.; Chan, K. S. *J. Org. Chem.* **1994**, *59*, 3585−3589. (b) Merlic, C. A.; Albaneze, J. *Tetrahedron Lett.* **1995**, *36*, 1007−1110.

(8) (a) Zora, M.; Herndon, J. W. *J. Org. Chem.* **1994**, *59*, 699−701. (b) Herndon, J. W.; Zhu, Y. *Tetrahedron Lett.* **1998**, *39*, 7443−7446. (c) Harvey, D. F.; Neil D. A. *Tetrahedron* **1993**, *49*, 2145−2150.

(9) Zora, M.; Herndon, J. W. *Organometallics* **1994**, *12*, 3370−3374. To our knowledge, this example and ref 1 are the only examples of C−C bond insertion by a discrete transition metal−carbene complex.

(10) Deoxgenations using low-valent chromium has precedent. (a) Tumer, S. U.; Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1992**, *114*, 8394−8404. (b) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060−1062.

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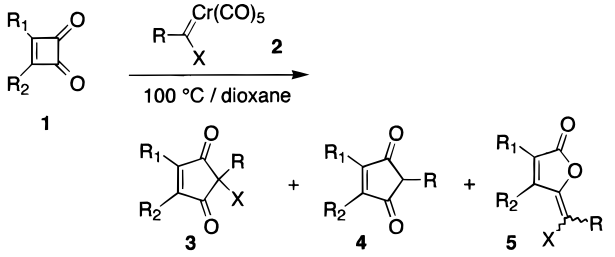
Table 1. Coupling of Cyclobutenediones with Fischer Carbene Complexes



cyclobutenediones	carbene complexes
A $R_1, R_2 = i$-PrO	**A** $R = CH_3$, $X = OCH_3$
B $R_1 = i$-PrO, $R_2 = CH_3$	**B** $R = CH_3$, $X = N(CH_3)_2$
C $R_1 = CH_3$, $R_2 = Ph$	**C** $R = c$-C_3H_5, $X = OCH_3$
D $R_1, R_2 = CH_3$	**D** $R = p$-CH_3OPh, $X = OCH_3$
	E $R = p$-CH_3Ph, $X = OCH_3$
	F $R = Ph$, $X = OCH_3$
	G $R = p$-$ClPh$, $X = OCH_3$
	H $R = p$-CF_3Ph, $X = OCH_3$

adducts **3**−**5** and **14**−**18**

A $R_1, R_2 = i$-PrO, $R = CH_3$, $X = OCH_3$ (**1A** + **2A**)
B $R_1, R_2 = i$-PrO, $R = CH_3$, $X = N(CH_3)_2$ (**1A** + **2B**)
C $R_1, R_2 = i$-PrO, $R = c$-C_3H_5, $X = OCH_3$ (**1A** + **2C**)
D $R_1, R_2 = i$-PrO, $R = Ph$, $X = OCH_3$ (**1A** + **2F**)
E $R_1 = i$-PrO, $R_2 = CH_3$, $R = CH_3$, $X = OCH_3$ (**1B** + **2A**)
F $R_1 = CH_3$, $R_2 = i$-PrO, $R = p$-CH_3OPh, $X = OCH_3$ (**1B** + **2D**)
G $R_1 = CH_3$, $R_2 = i$-PrO, $R = p$-CH_3Ph, $X = OCH_3$ (**1B** + **2E**)
H $R_1 = CH_3$, $R_2 = i$-PrO, $R = Ph$, $X = OCH_3$ (**1B** + **2F**)
I $R_1 = CH_3$, $R_2 = i$-PrO, $R = p$-$ClPh$, $X = OCH_3$ (**1B** + **2G**)
J $R_1 = CH_3$, $R_2 = i$-PrO, $R = p$-CF_3Ph, $X = OCH_3$ (**1B** + **2H**)
K $R_1 = CH_3$, $R_2 = Ph$, $R = CH_3$, $X = OCH_3$ (**1C** + **2A**)
L $R_1, R_2 = CH_3$, $R = p$-CF_3Ph, $X = OCH_3$ (**1D** + **2H**)

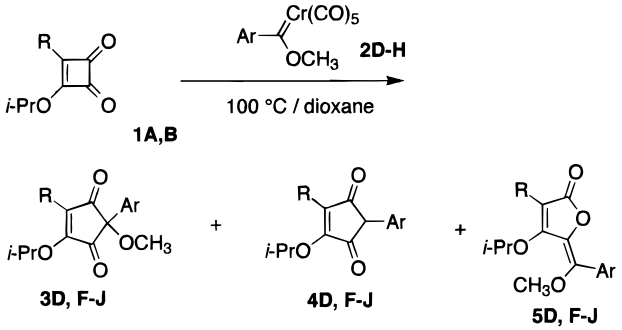
entry	cyclobutenedione	carbene complex	yield **3**	yield **4**	yield **5**[a]
A	**1A**	**2A**	31	14	0
B	**1A**	**2B**	12	0	0
C	**1A**	**2C**	34	17	0
D	**1A**	**2F**	0	0	55
E	**1B**	**2A**	25	16	0
F	**1B**	**2D**	37	30	11
G	**1B**	**2E**	29	27	15
H	**1B**	**2F**	20	21	14
I	**1B**	**2G**	19	23	22
J	**1B**	**2H**	15	15	29
K	**1C**	**2A**	20	15	0
L	**1D**	**2H**	8	7	0

[a] Combined yield of *E*- and *Z*-isomers; in all cases a nearly 1:1 *E*:*Z* mixture was obtained.

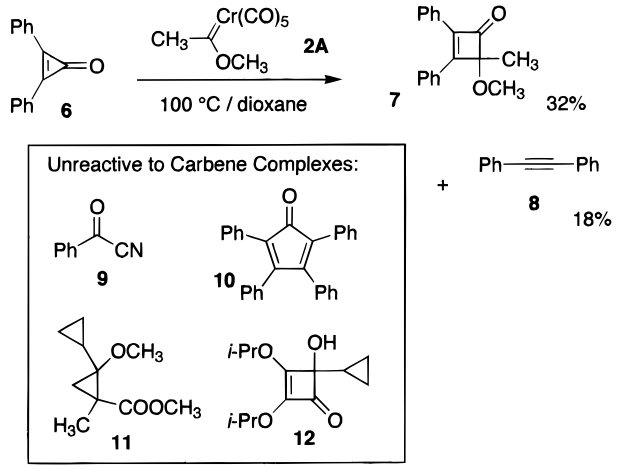
3B[11] only in low yield; this is the only case where the reduced cyclopentenedione **4** was not observed. In most cases, adducts were produced in good to moderate total yield; however much lower yields were observed in couplings involving nonoxygenated cyclobutenediones (entries K, L).

Coupling of Arylcarbene Complexes with Cyclobutenediones. The reaction of arylcarbene complexes and cyclobutenediones (entries D and F−J) afforded 5-alkylidenefuranone derivatives (**5**) and/or cyclopentenedione derivatives (**3** or **4**) (Scheme 2). Reaction of dioxygenated cyclobutenedione **1A** with phenylcarbene complex **2F** (entry D) afforded exclusively the 5-alkylidenefuranone derivative **5D** as a 1.1:1 *E*:*Z* mixture of alkene stereoisomers. The reaction of monooxygenated cyclobutenedione **1B** with a variety of arylcarbene complexes (entries F−J) afforded mixtures of cyclopentenediones **3** and **4** and alkylidenefuranones **5**. The cyclopentenedione/alkylidenefuranone ratio was insensitive to the reaction time, and neither the pure alkylidenefuranone nor the pure cyclopentenedione underwent interconversion under the reaction conditions.[12] Coupling of nonoxygenated cyclobutenedione **1D** with arylcarbene complex **2H** (entry L) afforded only cyclopentenediones **3L** and **4L** in low yield.

Scheme 2



Scheme 3



Reaction of Other Small-Ring Substrates with Carbene Complexes. A variety of other strained ring systems were tested in their reaction with carbene complex **2A**. Diphenylcyclopropenone (**6**) was the only compound that appeared to form a C−C bond insertion product (Scheme 3), and the reaction of this compound with a variety of carbene complexes has been reported.[9] Benzoyl cycanide (**9**) did not form an adduct with carbene complex **2A** in refluxing dioxane. Other strained ring-containing compounds, including tetraphenylcyclopentadienone (**10**), donor−acceptor-substituted cyclopropane **11**, and cyclobutenone **12**, did not form an adduct with carbene complex **2A**.

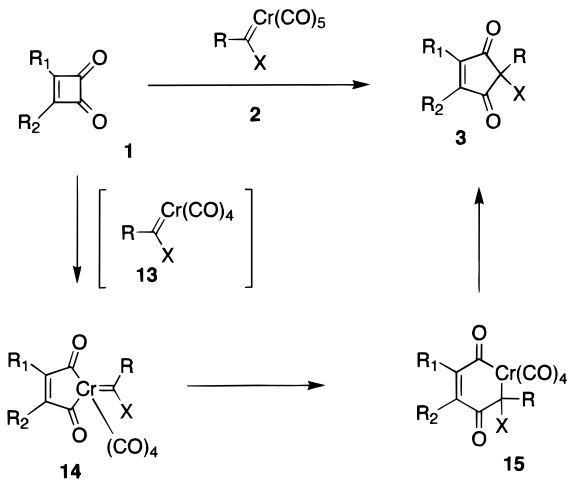
Discussion

Formation of Cyclopentenediones (3). The mechanism proposed for the formation of cyclopentenediones

(11) For an alternative synthesis of 2-amino-1,3-cyclopentenediones, see: Sun, L. J.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 6856−6858.

(12) (a) For interconversion via thermolysis, see: Claisen, L.; Ewan, T. *Justus Liebigs Ann. Chem.* **1895**, *284*, 245−299. (b) For interconversion via base, see: Gedge, D. R.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1978**, 880−882. (c) For utilization of this interconversion for organic synthesis, see: Campbell, A. C.; Maidment, M. S.; Pick, J. H.; Stevenson, D. F. M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1567−1576.

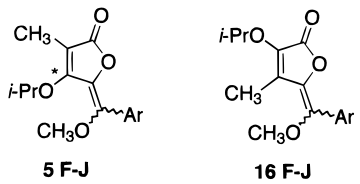
Scheme 4



is depicted in Scheme 4. First CO dissociation followed by oxidative addition[13] affords the metallacyclopentenedione **14**,[14] followed by acyl migration to afford metallacyclohexenedione **15**, which affords cyclopentenedione **3** upon reductive elimination. The reaction is inhibited by the addition of triphenylphosphine to the reaction mixture, which further supports this mechanism.

Formation of Deoxygenated Cyclopentenediones (4). The formation of deoxygenated cyclopentenediones (**4**) is a secondary reaction process and occurs via a chromium-induced reduction of cyclopentenedione **3**. When cyclopentenedione **3A** was an additive in the coupling of carbene complex **2C** with cyclobutenedione **1A**, partial conversion to deoxygenated cyclopentenedione **4A** was observed. Similarly, treatment of cyclopentenedione **3A** with chromium hexacarbonyl in refluxing dioxane led to a slow reduction to **4A**. Secondary deoxygenation processes have often been observed in the reactions of chromium carbene complexes.[10] A possible mechanism involves electron transfer followed by β-elimination. No deoxygenation was observed in the amino analogues (entry B) possibly due to the poorer leaving group ability of an amino group relative to an alkoxy group.

Structural Assignment of Alkylidenefuranones (5). A major concern in the structural assignment of the alkylidenefuranones **5F**−**H** is the placement of the isopropoxy group on the furanone ring system. Assignment as **5** and not **16** is based primarily on the severe chemical shift differences of the isopropoxy methyls and methines in the *E* and *Z* isomers of **5F**−**H**. In the *Z* isomers, the chemical shift of the isopropyl methyls is below δ 0.90 in all cases, while the same proton in the *E* isomers occurs at δ 1.40−1.42. Similarly, the isopropyl methines appear at δ 4.39−4.51 in the *Z* isomers and δ 4.83−4.88 in the *E* isomers. This large effect has been attributed to strong anisotropic interaction of the aromatic rings and the isopropoxy groups, which would be predicted for **5** and not **16**. The methyl group on the furanone ring occurs in the narrow chemical shift range of δ 1.90−2.01 on all the isomers of **5F**−**H**. Additional support for this structural assignment is from the carbon-13 NMR spectrum. Compounds **5F**−**J** all feature one carbon signal in the range 161.5−163.0, which is consistent with the asterisked carbon in the highly polarized β-alkoxy-α,β-unsaturated carbonyl linkage of **5F**−**J**.[15] The alkene carbons in the α-hydroxy-α,β-unsaturated ester system occur at less than δ 140.[16]



Formation of Alkylidenefuranones (5). The formation of alkylidenefuranones was observed only in the coupling of arylcarbene complexes with cyclobutenediones. The alkylidenefuranone was the exclusive product from the coupling of phenylcarbene complex **2F** with dioxygenated cyclobutenedione **1A**; however mixtures of alkylidenefuranones and cyclopentenediones were observed in the coupling of monooxygenated cyclobutenedione **1B** and arylcarbene complexes **2D**−**H**. Coupling of unoxygenated cyclobutenedione **1D** and arylcarbene complex **2H** afforded only cyclopentenediones **3L** and **4L** in low yield; no alkylidenefuranones were observed from this coupling. In all cases, the alkylidenefuranone was a nearly 1:1 mixture of *E*- and *Z*-stereoisomers.

The interconversion of cyclopentenediones and alkylidenefuranones is a well-documented process and can be induced by either base[12b] or thermolysis.[12a] The alkylidenefurane/cyclopentenedione ratio was insensitive to reaction time. Furthermore, the conversion of alkylidenefuranone **5H** to cyclopentenedione **3H** was not observed when **5H** was heated to 100 °C in dioxane or heated to 100 °C in dioxane in the presence of chromium hexacarbonyl, or when **5H** was an additive in the coupling of cyclobutenedione **1B** and methylcarbene complex **2A**. These results suggest that alkylidenefuranones are primary products of the coupling reaction and do not result from the rearrangement of cyclopentenediones under the conditions of the reaction.

A possible mechanism for the alkylidenefuranone formation is depicted in Scheme 5. Migration of the more electron-deficient acyl group in intermediate metallacyclopentenedione−carbenes **14F**−**J** affords the indicated regioisomer of metallacyclohexenediones **15F**−**J**. Elimination of chromium affords enolate−acylium intermediates **17F**−**J**, which undergo intramolecular O-acylation to afford the alkylidenefuranone.[17]

Electronic Dependence on the Alkylidenefuranone/Cyclopentenedione Ratio. There appears to be an electronic dependence on the alkylidenefuranone/cyclopentenedione ratio for entries F−J of Table 1 (see Table 2). More alkylidenefuranone is produced for the

(13) This C−C bond is very susceptible to oxidative addition. Liebeskind, L. S.; Jewell, C. F., Jr. *J. Organomet. Chem.* **1985**, *285*, 305−319.

(14) Similar intermediates have been proposed in unrelated processes. (a) Xu, Y.-C.; Challener, C. A.; Dragisch, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269−7271. (b) Liebeskind, L. S.; Chidambaran, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025−5026.

(15) Anderson, J. R.; Edwards, R. L.; Whalley, A. J. S. *J. Chem. Soc., Perkin Trans. 1* **1982**, 215−221.

(16) a. Raffauf, R. F.; Zennie, T. M.; Onan, K. D.; Le Quesne, P. W. *J. Org. Chem.* **1984**, *49*, 2714−2718.

(17) A similar explanation has been used to explain formation of cyclopentendiones and alkylidenefuranones in ring expansion of 4-diazoalkyl-2-cyclobuten-1-ones. Ohno, M.; Noda, M.; Yamamoto, Y.; Eguchi, S. *J. Org. Chem.* **1999**, *64*, 707−712.

Scheme 5

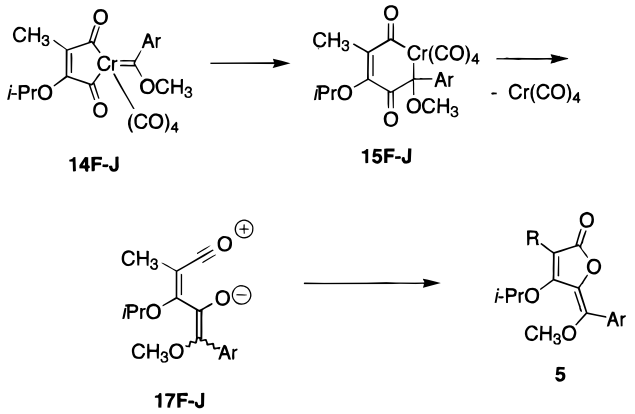


Table 2. Hammett Parameters for Entries F−J

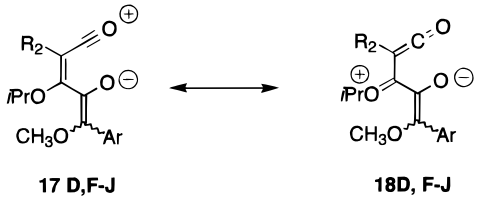
entry[a]	**3**+**4/5**	% **5x/5H** (log)[b]	σ	σ+
F	6.09	0.554 (−0.257)	−0.268	−0.648
G	3.73	0.831 (−0.082)	−0.170	−0.250
H	2.93	1.000 (0)	0	0
I	1.91	1.351 (0.125)	0.227	0.035
J	1.03	1.936 (0.284)	0.54	0.582

[a] The entry letters match those in Table 1. [b] The % **5x** is the % yield of **5x** divided by the sum of the % yields of **3x**, **4x**, and **5x**; the % **5H** is 25.4%.

carbene complexes featuring electron-deficient aromatic rings. A Hammett plot for log of % alkylidenefuranone Ar−X/Ar−H gives a ρ of 0.61 (correlation coefficient = 0.95) using σ values and 0.45 (correlation coefficient = 0.96) using σ^+ values.[18] The observed ρ values are supportive of the mechanism in Scheme 5, where there is significant negative charge development in the vicinity of the aryl group. Since α-aryl groups significantly enhance the acidity of ketones,[19] this could also explain the absence of alkylidenefuranones in the coupling of cyclobutenediones with alkylcarbene complexes **2A**−**C** (entries A−C, E, K). Alternatively, enolate−ketene **17** might be an intermediate in all of the reaction processes, and the alkylidenefuranone/cyclopentenedione ratios would thus reflect the O−Vs C-acylation ratios for the enolate species.

The structure of the cyclobutenedione starting material also has an effect on the product distribution. Only the alkylidenefuranone **5D** was obtained in the coupling of phenylcarbene complex **2F** with dioxygenated cyclobutenedione **1A** (entry D). Mixtures of alkylidenefuranones and cyclopentenediones were obtained from the coupling of arylcarbene complexes **2D**−**H** with monooxygenated cyclobutenedione **2D** (entries F−J), while only cyclopentenediones were obtained from the coupling of arylcarbene complex **2H** with unoxygenated cyclobutenedione **1D** (entry L). A possible rationale for the absence of alkylidenefuranone in entry L is the absence of resonance stabilization of the ketene species in **17L** by the oxygen substituent (exhibited by resonance structure **18** in Scheme 6). As noted in the comparison of entry D with entry H, the R_2 substituent also has a dramatic effect on the alkylidenefuranone/cyclopentenedione ratio. The rationale for this difference

Scheme 6



is less clear; when R_2 is isopropoxy, the ketene resonance is destabilized relative to the case where R_2 is methyl;[20] however the effect on the stability of the acylium ion is not clear.

Summary

The generality of the direct insertion of Fischer carbenes into the acyl−acyl bond of cyclobutenediones has been demonstrated in a variety of electronically diverse cyclobutenedione derivatives. The reaction leads to either cyclopentenediones[21] or alkylidenefuranone derivatives in moderate to good yield in a single step. A mechanism involving insertion of chromium into the acyl−acyl bond followed by acyl migration and reductive elimination was proposed. Alkylidenefuranone formation was attributed to ionization of the carbon−chromium bond of metallacyclohexenedione intermediate to form an enolate, and this process was supported through a Hammett study.

Experimental Section

General Considerations. Nuclear magnetic resonance (^{1}H and ^{13}C) spectra were recorded on a Bruker AF200 (200 MHz) or Bruker AF400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded on a Nicolet 5DXC FT-IR spectrometer. Band positions are reported in reciprocal centimeters (cm^{-1}). Band intensities are reported relative to the most intense band and are listed as br (broad), vs (very strong), s (strong), m (medium), w (weak). Mass spectra (MS) were obtained on a VG 7070E spectrometer using electron impact (EI) or chemical ionization (CI) or on a Hewlett- Packard GC-Mass Spec 5970B with mass selection detector; *m*/*e* values are reported, followed by the relative intensity in parentheses. Flash column chromatography was performed using thick-walled glass columns and "flash grade" silica (Bodmann 230−400 mesh). Routine thin-layer chromatography (TLC) was performed by using precoated 0.25 mm silica gel plates purchased from Whatman. The relative proportion of solvents in mixed chromatography solvents refers to the volume/volume ratio. All commercially available reagents and reactants were obtained in reagent grade and used without purification. All reaction solvents were distilled for purity. Diethyl ether, THF, and dioxane were distilled from sodium/benzophenone ketyl, and dichloromethane was distilled from calcium hydride prior to use. All reactions were performed in an inert atmosphere created by a slight positive pressure (ca. 0.1 psi) of nitrogen. Cyclobutenediones **1A**−**D** were prepared according to literature procedures.[22] Carbene complex **2C** was prepared according to a literature procedure.[10a]

(18) Gordon, A. J.; Ford, R. A. *The Chemist's Companion;* John Wiley and Sons: New York, 1972; pp 145−147.
(19) Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714−1718.
(20) Gong, L.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1991**, *113*, 6021−6028.
(21) For a general discussion of the synthesis and importance of cyclopentenediones, see refs 11, 12, 14, and 17.
(22) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482−2488.

General Procedure I. Preparation of Carbene Complexes. At − 78 °C and under nitrogen, a solution of *tert*-butyllithium (1.7 M in pentanes, 11.7 mL, 20.0 mmol) was added to a solution of corresponding alkyl bromide (10.0 mmol) in diethyl ether (25 mL) via syringe over a period of 15 min. The mixture was stirred for 30 min at −78 °C and then transferred via cannula to a suspension of metal hexacarbonyl (10.0 mmol) in diethyl ether (50 mL) at 0 °C. (If commercially available, the corresponding alkyllithium (10.0 mmol) was added directly to a suspension of metal hexacarbonyl (10.0 mmol) in diethyl ether (50 mL) at 0 °C under nitrogen over a period of 15 min.) The reaction mixture was allowed to warm to room temperature and then stirred for 1 h. The mixture was cooled to 0 °C and methyl trifluoromethanesulfonate (3.4 mL, 30 mmol) was added. The mixture was stirred at room temperature for 20 min. The reaction mixture was poured into saturated aqueous sodium bicarbonate solution in a separatory funnel and then extracted with hexane (3 × 100 mL). The hexane layer was washed with water and saturated aqueous sodium chloride solution, respectively. After drying over sodium sulfate, the solvent was removed on a rotary evaporator. The crude oil was purified by flash chromatography on silica gel using hexane as the eluent.

Pentacarbonyl[(methyl)methoxymethylene]chromium (2A). General procedure I was followed using methyllithium (6.7 mL of a 1.5 M diethyl ether solution, 10.00 mmol), chromium hexacarbonyl (2.200 g, 10.00 mmol), and methyl trifluoromethanesulfonate (3.4 mL, 30.00 mmol). After chromatographic purification, the yellow fraction was collected to give carbene complex **2A** (mp 33−34 °C, 1.400 g, 56%).

2A: ^{1}H NMR ($CDCl_3$) δ 5.35 (s, 3 H), 4.65 (s, 3 H); IR (CCl_4) 2064 (vs), 1985 (s), 1948 (vs) cm^{-1}. The spectral data are in agreement with those reported previously for this compound.[23] Since the acquisition of these data, we have verified that the more economical procedure using dimethyl sulfate as the methylating agent, developed by Wulff and co-workers,[24] is applicable to the synthesis of this carbene complex.

Pentacarbonyl[methyl(dimethylamino)methylene]chromium (2B). A solution of carbene complex **2A** (0.750 g, 3.00 mmol) and dimethylamine (0.38 mL of a 40 wt % solution in water, 3.00 mmol) in THF (25 mL) was stirred at room temperature for a period of 30 min. The mixture was stirred at room temperature for 30 min. The reaction mixture was poured into saturated aqueous sodium bicarbonate solution in a separatory funnel and then extracted with hexane. The hexane layer was washed with water and saturated aqueous sodium chloride solution, respectively. After drying over sodium sulfate, the solvent was removed on a rotary evaporator. The crude oil was purified by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as the eluent. The fraction was collected to give carbene complex **2B** (mp 74−75 °C, 0.570 g, 76%).

2B: ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3 H), 3.29 (s, 3 H), 2.67 (s, 3 H); IR (CCl_4) 2054 (vs), 1970 (vs), 1923 (vs) cm^{-1}. The spectral data are in agreement with those reported previously for this compound.[25]

Pentacarbonyl[(4-methoxyphenyl)methoxymethylene]chromium (2D). General procedure I was followed using 4-bromoanisole (1.87 g, 10.0 mmol), *tert*-butyllithium (11.7 mL of 1.7 M pentane solution, 20.0 mmol), chromium hexacarbonyl (2.20 g, 10.0 mmol), and methyl trifluoromethanesulfonate (3.4 mL, 30 mmol). After chromatographic purification, the red fraction was collected to give carbene complex **2D** (2.39 g, 70%).

2D: ^{1}H NMR ($CDCl_3$) δ 7.75−6.87 (m, 4 H), 4.84 (s, 3 H), 3.86 (s, 3 H). The spectral data are in agreement with those reported previously for this compound.[26]

Pentacarbonyl[(4-methylphenyl)methoxymethylene]chromium (2E). General procedure I was followed using 4-tolyl bromide (1.71 g, 10.0 mmol), *tert*-butyllithium (11.7 mL of 1.7 M pentane solution, 20.0 mmol), chromium hexacarbonyl (2.20 g, 10.0 mmol), and methyl trifluoromethanesulfonate (3.4 mL, 30 mmol). After chromatographic purification, the red fraction was collected to give carbene complex **2E** (2.28 g, 70%).

2E: ^{1}H NMR ($CDCl_3$) δ 7.36−7.17 (m, 4 H), 4,74 (s, 3 H), 2.37 (s, 3 H). The spectral data are in agreement with those reported previously for this compound.[26]

Pentacarbonyl[(phenyl)methoxymethylene]chromium (2F). General procedure I was followed using phenyllithium (5.6 mL of a 1.8 M cyclohexanes/ether solution, 10.0 mmol), chromium hexacarbonyl (2.20 g, 10.0 mmol), and methyl trifluoromethanesulfonate (3.4 mL, 30 mmol). After chromatographic purification, the red fraction was collected to give carbene complex **2F** (2.03 g, 65%).

2F: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 4.65 (s, 3 H); IR (Ccl_4) 2064 (vs), 1986 (m), 1951 (vs) cm^{-1}. The spectral data are in agreement with those reported previously for this compound.[26]

Pentacarbonyl[(4-chlorophenyl)methoxymethylene]chromium (2G). General procedure I was followed using 4-chlorobromobenzene (1.91 g, 10.0 mmol), *n*-butyllithium (6.25 mL of 1.6 M pentane solution, 10.0 mmol), chromium hexacarbonyl (2.20 g, 10.0 mmol), and methyl trifluoromethanesulfonate (3.4 mL, 30 mmol). After chromatographic purification, the red fraction was collected to give carbene complex **2G** (1.73 g, 50%).

2G: ^{1}H NMR ($CDCl_3$) δ 7.40−7.28 (m, 4 H), 4.77 (s, 3 H). The spectral data are in agreement with those reported previously for this compound.[26]

Pentacarbonyl[(4-trifluoromethylphenyl)methoxymethylene]chromium (2H). General procedure I was followed using 4-trifluoromethylbromobenzene (2.24 g, 10.0 mmol), *n*-butyllithium (6.25 mL of 1.6 M pentane solution, 10.0 mmol), chromium hexacarbonyl (2.20 g, 10.0 mmol), and methyl trifluoromethanesulfonate (3.4 mL, 30 mmol). After chromatographic purification, the red fraction was collected to give carbene complex **2H** (1.90 g, 50%).

2H: ^{1}H NMR ($CDCl_3$) δ 7.68−7.24 (m, 4 H), 4.72 (s, 3 H). The spectral data are in agreement with those reported previously for this compound.[26]

General Procedure II: Coupling of Carbene Complexes with Cyclobutenediones. Reaction of Carbene Complex 2F with 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione (1B). A solution of cyclobutenedione **1B** (1.00 mmol) and carbene complex **2F** (1.20 mmol) in dioxane (5 mL) was heated to reflux under nitrogen for a period of 4 h. The mixture was allowed to cool to room temperature, and the solvent was removed on a rotary evaporator. The residue was dissolved in 9:1 hexane/ethyl acetate (25 mL) and filtered through Celite. After removal of solvent on a rotary evaporator, final purification was achieved by flash chromatography on silica gel using 19:1 hexane/ethyl acetate as the eluent.

Reaction of Carbene Complex 2A with 3,4-Diisopropoxy-3-cyclobutene-1,2-dione (1A): Entry A of Table 1. General procedure II was followed using cyclobutenedione **1A** (0.198 g, 1.00 mmol) and carbene complex **2A** (0.325 g, 1.30 mmol). After chromatographic purification, two fractions were isolated. The product in the first fraction was assigned as 4,5-diisopropoxy-2-methyl-4-cyclopentene-1,3-dione (**4A**) (0.032 g, 14%). The product in the second fraction was identified as 4,5-diisopropoxy-2-methoxy-2-methyl-4-cyclopentene-1,3-dione (**3A**) (0.080 g, 31%).

3A: ^{1}H NMR ($CDCl_3$) δ 5.48 (septet, 2 H, J = 6.1 Hz), 3.18 (s, 3 H), 1.35 (s, 3 H), 1.32 (d, 6 H, J = 6.1 Hz), 1.31 (d, 3 H,

(23) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445−2446.
(24) Bao, J.; Wulff, W. D.; Dominy, J. B.; Fumo, M. J.; Grant, E. B.; Rob, A. C.; Whitcomb, M. C.; Yeung, S.-M.; Ostrander, R. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 3392−3405.
(25) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *13*, 387−398.
(26) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237−258.

J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 194.9, 150.1, 77.3, 74.8, 53.2, 22.9, 19.2; IR ($CDCl_3$): 1688 (vs), 1601 (vs) cm^{-1}; MS (EI) 256 (M+, 25), 214 (59), 172 (100), 143 (24), 115 (21), 97 (13), 84 (10), 75 (10), 69 (10), 55 (30); HRMS calcd for $C_{13}H_{20}O_5$ 256.1311, found 256.1301.

4A: ^{1}H NMR ($CDCl_3$) δ 5.41 (septet, 2 H, J = 6.1 Hz); 2.71 (q, 1 H, J = 7.5 Hz), 1.31 (d, 12 H, J = 6.1 Hz), 1.20 (d, 3 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 195.9, 149.9, 74.3, 44.8, 22.9, 11.2; IR ($CDCl_3$) 1685 (vs), 1609 (m) cm^{-1}; MS (EI) 226 (M+, 10), 184 (37), 153 (31), 142 (51), 114 (100), 73 (17), 68 (28); HRMS calcd for $C_{12}H_{18}O_4$ 226.1205, found 226.1220.

Reaction of Carbene Complex 2B with 3,4-Diisopropoxy-3-cyclobutene-1,2-dione (1A): Entry B of Table 1. General procedure II was followed using cyclobutenedione **1A** (0.198 g, 1.00 mmol) and carbene complex **2B** (0.342 g, 1.30 mmol). After chromatographic purification, a single fraction was isolated and identified as 4,5-diisopropoxy-2-methyl-2-(*N*,*N*-dimethylamino)-4-cyclopentene-1,3-dione (**3B**) (0.033 g, 12%).

3B: ^{1}H NMR ($CDCl_3$) δ 5.41 (septet, 2 H, J = 6.1 Hz), 2.34 (s, 6 H), 1.30 (s, 3 H), 1.27 (d, 12 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 198.8, 148.8, 74.4, 65.3, 40.0, 23.0, 22.9, 18.7; IR ($CDCl_3$) 1681 (vs), 1604 (s) cm^{-1}; MS (EI) 269 (M+, 67), 227 (34), 216 (68), 198 (57), 185 (26), 174 (100), 145 (23), 128 (83), 112 (36), 100 (31); HRMS calcd for $C_{14}H_{23}NO_4$ 269.1627, found 269.1629.

Reaction of Carbene Complex 2C with 3,4-Diisopropoxy-3-cyclobutene-1,2-dione (1A): Entry C of Table 1. General procedure II was followed using cyclobutenedione **1A** (0.198 g, 1.00 mmol) and carbene complex **2C** (0.359 g, 1.30 mmol). After chromatographic purification, two fractions were isolated. The product in the first fraction was assigned as 2-cyclopropyl-4,5-diisopropoxy-4-cyclopentene-1,3-dione (**4C**) (0.043 g, 17%). The product in the second fraction was identified as 2-cyclopropyl-4,5-diisopropoxy-2-methoxy-4-cyclopentene-1,3-dione (**3C**) (0.096 g, 34%).

3C: ^{1}H NMR ($CDCl_3$) δ 5.47 (septet, 2 H, J = 6.1 Hz), 3.27 (s, 3 H), 1.33 (d, 6 H, J = 6.1 Hz), 1.32 (d, 6 H, J = 6.1 Hz), 1.23 (m, 1 H), 0.56−0.48 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 193.5, 150.8, 79.8, 74.8, 53.4, 22.9, 14.6, 1.9; IR ($CDCl_3$) 1685 (vs), 1601 (vs) cm^{-1}; MS (EI) 282 (M+, 37), 251 (15), 240 (89), 209 (14), 198 (100), 183 (13), 168 (14), 155 (10), 142 (24), 125 (23), 110 (44); HRMS calcd for $C_{15}H_{22}O_5$ 282.1467, found 282.1467.

4C: ^{1}H NMR ($CDCl_3$) δ 5.40 (septet, 2 H, J = 6.1 Hz), 2.46 (d, 1 H, J = 6.5 Hz), 1.35 (d, 6 H, J = 6.1 Hz), 1.34 (d, 6 H, J = 6.1 Hz), 0.98 (m, 1 H), 0.52−0.43 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 194.5, 150.4, 74.3, 50.5, 22,9, 9.6, 1.8; IR ($CDCl_3$) 1686 (vs), 1612 (s) cm^{-1}; MS (EI) 252 (M+, 16), 227 (6), 210 (73), 195 (8), 184 (5), 168 (100), 150 (6), 140 (37), 122 (22), 111 (22); HRMS calcd for $C_{14}H_{20}O_4$ 252.1361, found 252.1346.

Reaction of Carbene Complex 2F with 3,4-Diisopropoxy-3-cyclobutene-1,2-dione (1A): Entry D of Table 1. General procedure II was followed using cyclobutenedione **1A** (0.198 g, 1.00 mmol) and carbene complex **2F** (0.406 g, 1.30 mmol). After chromatographic purification, two fractions were isolated. The product in the first fraction was assigned as compound **5D-*E*** (0.093 g, 29%). The product in the second fraction was identified as compound **5D-*Z*** (0.083 g, 26%).

5D-*E*: ^{1}H NMR ($CDCl_3$) δ 7.64 (d, 2 H, J = 7.1 Hz), 7.36−7.28 (m, 3 H), 5.16 (septet, 1 H, J = 6.1 Hz), 4.89 (septet, 1 H, J = 6.1 Hz), 3.55 (s, 3 H), 1.35 (d, 6 H, J = 6.1 Hz), 1.24 (d, 6 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 164.5, 150.3, 143.2, 134.5, 131.8, 130.5, 128.8, 128.4, 122.8, 74.4, 73.7, 60.5, 22.7, 22.5; IR ($CDCl_3$) 1748 (vs), 1626 (s) cm^{-1}; MS (EI) 318 (M+, 56), 276 (64), 234 (100), 191 (57), 177 (27), 161 (27), 146 (22), 105 (30), 77 (19); HRMS calcd for $C_{18}H_{22}O_5$ 318. 1467, found 318.1477.

5D-*Z*: ^{1}H NMR ($CDCl_3$) δ 7.35−7.25 (m, 5 H), 4.82 (septet, 2 H, J = 6.1 Hz), 3.57 (s, 3 H), 1.18 (d, 6 H, J = 6.1 Hz), 0.84 (d, 6 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 164.3, 149.7, 141.9, 131.0, 130.5, 129.5, 128.3, 127.6, 121.4, 73.7, 73.5, 58.4, 22.5, 21.9; IR ($CDCl_3$) 1746 (vs), 1628 (s) cm^{-1}; MS (EI) 318 (M+, 100), 276 (50), 234 (64), 191 (36), 177 (19), 161 (18), 146 (13), 105 (22), 77(10); HRMS calcd for $C_{18}H_{22}O_5$ 318. 1467, found 318.1511. Compound 5F-*Z* was assigned as the *Z* isomer because of the upfield shift of an isopropyl secondary H (δ 4.82 in the *Z* isomer versus δ 5.16 and 4.89 in the *E* isomer) and methyl (δ 0.84 and 1.18 in the *Z* isomer versus δ 1.24 and 1.35 in the *E* isomer) and might be attributed to anisotropic interaction with the phenyl ring.

Reaction of Carbene Complex 2A with 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione (1B): Entry E of Table 1. General procedure II was followed using cyclobutenedione **1B** (0.154 g, 1.00 mmol) and carbene complex **2A** (0.325 g, 1.30 mmol). After chromatographic purification, two fractions were isolated. The product in the first fraction was assigned as 4-isopropoxy-2,5-dimethyl-4-cyclopentene-1,3-dione (**4E**) (0.030 g, 16%). The product in the second fraction was identified as 4-isopropoxy-2-methoxy-2,5-dimethyl-4-cyclopentene-1,3-dione (**3E**) (0.054 g, 25%).

3E: ^{1}H NMR ($CDCl_3$) δ 5.59 (septet, 1 H, J = 6.1 Hz), 3.16 (s, 3 H), 1.87 (s, 3 H), 1.31 (s, 3 H), 1.30 (d, 3 H, J = 6.1 Hz), 1.27 (d, 3 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 199.0, 198.5, 164.3, 137.2, 77.8, 74.8, 53.3, 23.2, 23.1, 19.1, 7.0; IR ($CDCl_3$) 1689 (vs), 1608 (s) cm^{-1}; MS (EI) 212 (M+, 100), 181 (10), 170 (88), 153 (49), 140 (29), 131 (11), 119 (8), 112 (18); HRMS calcd for $C_{11}H_{16}O_4$ 212.1048, found 212.1047.

4E: ^{1}H NMR ($CDCl_3$) δ 5.49 (septet, 1 H, J = 6.1 Hz), 2.66 (q, 1 H, J = 7.6 Hz), 1.84 (s, 3 H), 1.28 (d, 3 H, J = 6.1 Hz), 1.27 (d, 3 H, J = 6.1 Hz), 1.17 (d, 3 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 200.2, 199.2, 164.8, 136.4, 74.3, 45.7, 23.2, 23.1, 10.9, 7.0; IR ($CDCl_3$) 1689 (vs), 1616 (s) cm^{-1}; MS (EI) 182 (M+, 37), 166 (6), 153 (20), 149 (7), 141 (58), 140 (100), 122 (26), 111 (19); HRMS calcd for $C_{10}H_{14}O_3$ 182.0943, found 182.0948.

Reaction of *p*-Methoxyphenylcarbene Complex 2D with 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione (1B): Entry F of Table 1. General procedure II was followed using cyclobutenedione **1B** (0.154 g, 1.00 mmol) and carbene complex **2D** (0.410 g, 1.20 mmol). After chromatographic purification, four fractions were isolated. The product in the first fraction was assigned as compound **3F** (0.112 g, 37%). The product in the second fraction was identified as compound (**4F**) (0.083 g, 30%). The products in the third and fourth fractions were assigned as compounds **5F-*E*** (0.02 1 g, 7%) and **5F-*Z*** (0.012 g, 4%).

3F: ^{1}H NMR ($CDCl_3$) δ 7.36−6.83 (m, 4 H), 5.62 (septet, 1 H, J = 6.1 Hz), 3.76 (s, 3 H), 3.32 (s, 3 H), 1.95 (s, 3 H), 1.36 (d, 3 H, J = 6.1 Hz), 1.24 (d, 3 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 196.9, 195.8, 165.2, 160.1, 138.4, 128.6, 126.0, 114.0, 81.3, 75.0, 55.3, 53.9, 23.2, 7.2; IR (CH_2Cl_2) 1691 (vs), 1610 (s) cm^{-1}; MS (EI) 304 (M+, 13), 262 (31), 189 (22), 166 (21), 135 (100), 77 (26); HRMS calcd for $C_{17}H_{20}O_5$ 304.1311, found 304.1306.

4F: ^{1}H NMR ($CDCl_3$) δ 7.06−6.82 (m, 4 H), 5.58 (septet, 1 H, J = 5.9 Hz), 3.86 (s, 1 H), 3.75 (s, 3 H), 1.96 (s, 3 H), 1.35 (d, 3 H, J = 5.9 Hz), 1.32 (d, 3 H, J = 5.9 Hz); ^{13}C NMR ($CDCl_3$) δ 197.5, 196.4, 166.0, 159.2, 138.5, 129.3, 125.2, 114.4, 74.6, 56.2, 55.2, 23.1, 7.3; IR (CH_2C1_2) 1692 (vs), 1615 (s) cm^{-1}; MS (EI) 274 (M+, 100), 232 (53), 159 (7), 148 (76), 121 (62), 77 (8); HRMS calcd for $C_{16}H_{18}O_4$ 274.1205, found 274.1209.

5F-*E*: ^{1}H NMR ($CDCl_3$) δ 7.70−6.90 (m, 4 H), 4.84 (septet, 1 H, J = 6.1 Hz), 3.79 (s, 3 H), 3.62 (s, 3 H), 1.98 (s, 3 H), 1.40 (d, 6 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.5, 163.0, 160.6, 143.0, 135.5, 130.5, 124.2, 114.0, 103.0, 75.1, 60.6, 55.3, 22.6, 8.8; IR (CH_2C1_2) 1751 (vs), 1604 (s) cm^{-1} ; MS (EI) 304 (M+, 65), 262 (27), 189 (17), 166 (16), 135 (100), 77 (14); HRMS calcd for $C_{17}H_{20}O_5$ 304.1311, found 304.1308.

5F-*Z*: ^{1}H NMR ($CDCl_3$) δ 7.32−6.87 (m, 4 H), 4.40 (septet, 1 H, J = 6.1 Hz), 3.83 (s, 3 H), 3.65 (s, 3 H), 1.90 (s, 3 H), 0.89 (d, 6 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.6, 162.1, 160.9, 142.3, 132.0, 129.1, 123.5, 113.2, 100.7, 73.9, 58.5, 55.4, 21.9, 8.9; IR (CH_2C1_2) 1744 (vs), 1605 (vs) cm^{-1}; MS (EI) 304 (M+, 42), 262 (17), 189 (14), 166 (16), 135 (100), 83 (43); HRMS calcd

for $C_{17}H_{20}O_5$ 304.1311, found 304.1299. Compound **5C-*Z*** was assigned as the *Z* isomer because of the upfield shift of an isopropyl secondary H (δ 4.40 in the *Z* isomer versus δ 4.84 in the *E* isomer) and methyl (δ 0.89 in the *Z* isomer versus δ 1.40 in the *E* isomer) and might be attributed to anisotropic interaction with the phenyl ring.

Reaction of *p*-Tolylcarbene Complex 2E with 3-Isopropoxy-4-methyl-3-cyclobutene-l,2-dione (1B): Entry G of Table 1. General procedure II was followed using cyclobutenedione **1B** (0.154 g, 1.00 mmol) and carbene complex **2E** (0.391 g, 1.20 mmol). After chromatographic purification, four fractions were isolated. They were assigned as **3G** (0.083 g, 29%), **4G** (0.069 g, 27%), **5G-*E*** (0.023 g, 8%), and **5G-*Z*** (0.019 g, 7%).

3G: ^{1}H NMR ($CDCl_3$) δ 7.30−7.11 (m, 4 H), 5.62 (septet, 1 H, J = 6.1 Hz), 3.34 (s, 3 H), 2.3 (s, 3 H), 1.96 (s, 3 H), 1.36 (d, 3 H, J = 6.1 Hz), 1.25 (d, 3 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 196.8, 195.7, 165.4, 138.9,138.6, 131.2, 129.2, 127.0, 81.8, 75.0, 53.9, 23.2, 21.1, 7.2; IR (CH_2C1_2) 1691 (vs), 1612 (s) cm^{-1}; MS (EI) 288 (M+, 32), 246 (17), 216 (5), 189 (9), 173 (18), 135 (10), 119 (100), 91(39), 83 (45), 65 (16); HRMS calcd for $C_{17}H_{20}O_4$ 288.1362, found 288.1363.

4G: ^{1}H NMR ($CDCl_3$) δ 7.14−6.98 (m, 4 H), 5.57 (septet, 1 H, J = 6.1 Hz), 3.89 (s, 3 H), 2.29 (s, 3 H), 1.97 (s, 3 H), 1.35 (d, 3 H, J = 6.1 Hz), 1.32 (d, 3 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 197.3, 196.3, 166.1, 138.6, 137.6, 130.2, 129.6, 128.1, 74.7, 56.7, 23.2, 21.1, 7.3; IR (CH_2C1_2) 1693 (vs), 1618 (s) cm^{-1}; MS (EI) 258 (M+, 78), 216 (50), 159 (3), 132 (100), 105 (74), 78 (9); HRMS calcd for $C_{16}H_{18}O_3$ 258.1256, found 258.1254.

5G-*E*: ^{1}H NMR ($CDCl_3$) δ 7.63−7.18 (m, 4 H), 4. 83 (septet, 1 H, J = 6.1 Hz), 3.61 (s, 3 H), 2.36 (s, 3 H), 1.98 (s, 3 H), 1.41 (d, 6 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.4, 163.0, 143.1, 139.8, 136.0, 129.2, 128.9, 128.8, 103.4, 75.1, 60.5, 22.6, 21.4, 8.7; IR (CH_2C1_2) 1753 (vs), 1608 (s) cm^{-1}; MS (EI) 288 (M+, 33), 246 (22), 216 (10), 189 (9), 173 (27), 132 (13), 119 (100), 91(38), 83 (47), 65 (15); HRMS calcd for $C_{17}H_{20}O_4$ 288.1362, found 288.1373.

5G-*Z*: ^{1}H NMR ($CDCl_3$) δ 7.27−7.15 (m, 4 H), 4.39 (septet, 1 H, J = 6.0 Hz), 3.64 (s, 3 H), 2.38 (s, 3 H), 1.90 (s, 3 H), 0.86 (d, 6 H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 170.1, 162.1, 142.7, 139.8, 130.5, 128.5, 100.5, 73.9, 58.4, 21.8, 21.4, 8.9; IR (CH_2-$C1_2$) 1748 (vs), 1609 (s) cm^{-1}; MS (EI) 288 (M+, 72), 246 (32), 189 (12), 173 (22), 119 (100), 91(34); HRMS calcd for $C_{17}H_{20}O_4$ 288.1362, found 288.1364.

Reaction of Phenylcarbene Complex 2F with 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione (1B): Entry H of Table 1. General procedure II was followed using cyclobutenedione **1B** (0.154 g, 1.00 mmol) and carbene complex **2F** (0.375 g, 1.20 mmol). After chromatographic purification, four fractions were isolated. They were assigned as **3H** (0.050 g, 20%), **4H** (0.046 g, 21%), **5H-*E*** (0.020 g, 7%), and **5H-*Z*** (0.020 g, 7%).

3H: ^{1}H NMR ($CDCl_3$) δ 7.45−7.30 (m, 511), 5.62 (septet, 111, J = 6.1 Hz), 3.35 (s, 3 H), 1.97 (s, 3 H), 1.36 (d, 3 H, J = 6.1 Hz), 1.25 (d, 3 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 196.6, 195.6, 165.6, 138.9, 134.3, 128.9, 128.6, 127.0, 82.0, 75.1, 54.0, 23.1, 7.2; IR ($CDCl_4$) 1697 (vs), 1618 (s) cm^{-1}; MS (EI) 274 (M+, 93), 243 (10), 233 (7), 217 (8), 202 (10), 175 (11), 159 (33), 148 (12), 121 (16), 120 (20), 105 (100); HRMS calcd for $C_{16}H_{18}O_4$ 274.1205, found 274.1204.

4H: ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 311), 7.11 (m, 2 H), 5.58 (septet, 1 H, J = 6.1 Hz), 3.92(s, 1 H), 1.97 (s, 311), 1.35 (d, 311, J = 6.1 Hz), 1.32 (d, 311, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 197.1, 196.0,166.1, 138.7, 133.2, 128.9, 128.3, 127.8, 74.7, 56.9, 23.1, 7.3; IR ($CDCl_4$) 1696 (vs), 1621 (s) cm^{-1}; MS (EI) 244 (M+, 100), 202 (41), 163 (8), 129 (6), 119 (16), 118 (52), 113 (7); HRMS calcd for $C_{15}H_{15}O_3$ 244.1099, found 244.1107.

5H-*E*: ^{1}H NMR ($CDCl_3$) δ 7.71 (m, 211), 7.33 (m, 3 H), 4.84 (septet, 1 H, J = 6.1 Hz), 3.62 (s, 311), 1.98 (s, 311), 1.41 (d, 611, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.3, 163.0, 142.9 136.4, 31.8, 129.5, 128.9, 128.5, 103.6, 75.2, 60.5, 22.7, 8.8; IR ($CDCl_4$) 1750 (vs), 1611 (s) cm^{-1}; MS (EI) 274 (M+, 100), 232 (50), 217 (8), 202 (9), 175 (10), 159 (30), 148 (10), 121 (15), 120 (18), 105 (99); HRMS calcd for $C_{16}H_{18}O_4$ 274.1205, found 274.1205.

5H-*Z*: ^{1}H NMR ($CDCl_3$) δ 7.50−7.30 (m, 511), 4.41 (septet, 111, J = 6.1 Hz), 3.66 (s, 311), 1.90 (s, 311), 0.84 (d, 611, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.0, 162.0, 142.4, 131.5, 130.5, 129.6, 127.8, 100.3, 73.8, 58.5, 21.8, 8.9; IR (CDCl4) 1744 (vs), 1611 (s) cm^{-1}; MS (EI) 274 (M+, 94), 232 (45), 217 (8), 202 (8), 175 (9), 159 (26), 148 (10), 137 (6), 121 (12), 120 (17), 105 (100); HRMS calcd for $C_{16}H_{18}O_4$ 274.1205, found 274.1187.

Reaction of *p*-Chlorophenylcarbene Complex 2G with 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione (1B): Entry I of Table 1. General procedure II was followed using cyclobutenedione **1B** (0.154 g, 1.00 mmol) and carbene complex **2G** (0.416 g, 1.20 mmol). After chromatographic purification, four fractions were isolated. They were assigned as **3I** (0.057 g, 19%), **4I** (0.063 g, 23%), **5I-*E*** (0.040 g, 13%), and **5I-*Z*** (0.029 g, 9%).

3I: ^{1}H NMR ($CDCl_3$) δ 7.33−7.32 (m, 4 H), 5.63 (septet, 1 H, J = 6.1 Hz), 3.33 (s, 3 H), 1.98 (s, 3 H), 1.37 (d, 3 H, J = 6.1 Hz), 1.27 (d, 3 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 196.2, 195.2, 182.6, 139.2, 135.2, 132.8, 128.9, 128.5, 81.3, 75.3, 54.0, 23.2, 7.3; IR (CH_2Cl_2) 1691 (vs), 1611 (s) cm^{-1}; MS (EI) 308 (M+, 100), 266 (58), 236 (10), 195 (9), 139 (5), 111 (8), 51(4); HRMS calcd for $C_{16}H_{17}O_4{}^{35}C1$ 308.0815, found 308.0802.

4I: ^{1}H NMR($CDCl_3$) δ 7.32−7.05 (m, 4 H), 5.58 (septet, 1 H, J = 5.6 Hz), 3.91 (s, 3 H), 1.97 (s, 3 H), 1.36 (d, 3 H, J = 5.6 Hz), 1.33 (d, 3 H, J = 5.6 Hz); ^{13}C NMR ($CDCl_3$) δ 196.6, 195.5, 156.0, 138.7, 133.9, 131.5, 129.7, 129.0, 74.9, 56.1, 23.2, 7.4; IR (CH_2Cl_2) 1682 (vs), 1615 (s) cm^{-1}; MS (EI) 278 (M+, 52), 236 (58), 163 (10), 152 (100), 125 (40), 89 (21), 63 (4); HRMS calcd for $C_{15}H_{15}O_3{}^{35}C1$ 278.0710, found 278.0702.

5I-*E*: ^{1}H NMR($CDCl_3$) δ 7.67 (d, 2 H, J = 8.7 Hz), 7.37 (d, 2 H, J = 8.7 Hz), 4.85 (septet, 1 H, J = 6.1 Hz), 3.63 (s, 3 H), 1.99 (s, 3 H), 1.40 (d, 6 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.1, 162.8, 141.5, 136.9, 135.5, 130.5, 130.1, 128.8, 103.5, 75.1, 60.8, 22.7, 8.9; IR (CH_2Cl_2) 1759 (s), 1613 (s) cm^{-1}; MS (EI) 308 (M+, 44), 266 (26), 193 (27), 181 (49), 169 (44), 139 (100), 131 (96), 119 (79), 83 (76), 69 (331); HRMS calcd for $C_{16}H_{17}O_4{}^{35}C1$ 308.0815, found 308.0820.

5I-*Z*: ^{1}H NMR($CDCl_3$) δ 7.36−7.29 (m, 4 H), 4.49 (septet, 1 H, J = 6.1 Hz), 3.68 (s, 3 H), 1.91 (s, 3 H), 0.90 (d, 6 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 169.9, 161.5, 141.0, 135.7, 131.8, 130.1, 128.3, 128.0, 99.9, 73.9, 58.9, 22.0, 9.0; IR (CH_2C1_2) 1749 (s), 1616 (m) cm^{-1}; MS (EI) 308 (M+, 44), 266 (27), 193 (27), 141 (37), 139 (100), 131 (37), 119 (32), 69 (123); HRMS calcd for $C_{16}H_{17}O_4{}^{35}C1$ 308.0815, found 308.0829.

Reaction of *p*-Trifluoromethylphenylcarbene Complex 2H with 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione (1B): Entry J of Table 1. General procedure II was followed using cyclobutenedione **1B** (0.154 g, 1.00 mmol) and carbene complex **2H** (0.456 g, 1.20 mmol). After chromatographic purification, four fractions were isolated. They were assigned as **3J** (0.051 g, 15%), **4J** (0.047 g, 15%), **5J-*E*** (0.045 g, 16%), and **5J-*Z*** (0.037 g, 13%).

3J: ^{1}H NMR ($CDCl_3$) δ 7.62−7.49 (m, 4 H), 5.64 (septet, 1 H, J = 6.1 Hz), 3.35 (s, 3 H), 2.00 (s, 3 H), 1.38 (d, 3 H, J = 6.1 Hz), 1.28 (d, 3 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 195.9, 194.9, 165.9, 139.7, 138.3, 127.4, 125.6, 125.6, 81.6, 75.5, 54.1, 23.2, 7.4; IR (CH_2Cl_2) 1693 (vs), 1610 (s) cm^{-1}; MS (EI) 324 (M+, 10), 300 (9), 270 (4), 255 (7), 227 (13), 173 (100), 145 (34), 111 (28); HRMS calcd for $C_{17}H_{17}F_3O_4$ 342.1079, found 342.1083.

4J: ^{1}H NMR ($CDCl_3$) δ 7.66−7.24 (m, 4 H), 5.59 (septet, 1 H, J = 5.0 Hz), 4.01 (s, 3 H), 1.99 (s, 3 H), 1.36 (d, 3 H, J = 5.0 Hz), 1.33 (d, 3 H, J = 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ 196.1, 195.1, 166.1, 138.8, 136.9, 128.8, 125.8, 75.0, 56.5, 23.2, 16.9, 7.4; IR (CH_2C1_2) 1694 (s), 1622 (m) cm^{-1}; MS (CI) 313 (M+, 29), 271 (40), 241 (8), 187 (100), 159 (55), 97 (12), 57 (23); HRMS calcd for $C_{16}H_{16}F_3O_3$ 313.1052, found 313.1060.

5J-*E*: ^{1}H NMR ($CDCl_3$) 87.88−7.62 (m, 4 H), 4.88 (septet, 1 H, J = 6.1 Hz), 3.62 (s, 3 H), 2.01 (s, 3 H), 1.42 (d, 6 H, J =

6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 169.9, 162.7, 140.9, 137.8, 135.7, 129.0, 125.4, 125.4, 103.7, 75.2, 60.8, 22.7, 8.9; IR (CH_2C1_2) 1761 (s), 1634 (m), 1613 (m) cm^{-1}; MS (EI) 342 (M+, 54), 300 (46), 270 (8), 227 (21), 173 (100), 126 (3); HRMS calcd for $C_{17}H_{17}F_3O_4$ 342.1079, found 342.1076.

5J-*Z*: ^{1}H NMR ($CDCl_3$) δ 7.66−7.47 (m, 4 H), 4.51 (septet, 1 H, J = 6.0 Hz), 3.72 (s, 3 H), 1.92 (s, 3 H), 0.86 (d, 6 H, J = 6.0 Hz).

Reaction of Carbene Complex 2A with 3-Methyl-4-phenyl-3-cyclobutene-1,2-dione (1C): Entry K of Table 1. General procedure II was followed using cyclobutenedione **1C** (0.172 g, 1.00 mmol) and carbene complex **2A** (0.325 g, 1.30 mmol). After chromatographic purification, two fractions were isolated. The product in the first fraction was assigned as 2,4-diinethyl-5-phenyl-4-cyclopentene-1,3-dione (**4K**) (0.031 g, 15%). The product in the second fraction was identified as 2-methoxy-2,4-diinethyl-5-phenyl-4-cyclopentene-1,3-dione (**3K**) (0.047 g, 20%).

3K: ^{1}H NMR ($CDCl_3$) δ 7.60−7.40 (m, 5 H), 3.28 (s, 3 H), 2.22 (s, 3 H), 1.43 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 203.6, 201.6, 152.7, 152.1, 130.4, 129.6, 128.6, 128.3, 76.3, 53.6, 18.9, 10.6; IR (CCl_4) 1709 (vs) cm^{-1}; MS (EI) 230 (M+, 100), 215 (18), 187 (20), 173 (8), 159 (7), 143 (5), 115 (30); HRMS calcd for $C_{14}H_{14}O_3$ 230.0943, found 230.0942.

4K: ^{1}H NMR ($CDCl_3$) δ 7.60−7.40 (m, 5 H), 2.81 (q, 1 H, J = 7.6 Hz), 2.18 (s, 3 H), 1.31 (d, 3 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 204.2, 202.6, 153.6, 153.1, 129.9, 129.5, 129.3, 128.5, 44.8, 10.7, 10.4; IR (CCl_4) 1702 (vs) cm^{-1}; MS (EI): 200 (M+, 100), 172 (11), 157 (9), 144 (13), 129 (4), 116 (52), 115 (69); HRMS calcd for $C_{13}H_{12}O_2$ 200.0837, found 200.0838.

Reaction of *p*-Trifluoromethylphenylcarbene Complex 2H with 3,4-Dimethyl-3-cyclobutene-1,2-dione (1D): Entry L of Table 1. General procedure II was followed using cyclobutenedione **1D** (0.110 g, 1.00 mmol) and carbene complex **2H** (0.456 g, 1.20 mmol). After chromatographic purification, two fractions were isolated. They were assigned as **3L** (0.024 g, 8%) and **4L** (0.019 g, 7%).

3L: ^{1}H NMR ($CDCl_3$) δ 7.59 (d, 2 H, J = 9.5 Hz), 7.49 (d, 2 H, J = 9.5 Hz), 3.34 (s, 3 H), 2.11 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 199.6, 156.3, 137.9, 127.7, 125.6, 125.6, 79.2, 54.2, 9.7; IR (CH_2Cl_2) 1700 (s) cm^{-1}; MS (EI) 298 (M+, 52), 174 (100), 145 (40), 69 (18), 54 (12); HRMS calcd for $C_{15}H_{13}F_3O_3$ 298.0817, found 298.0823.

4L: ^{1}H NMR ($CDCl_3$) δ 7.58 (d, 2 H, J = 8.6 Hz), 7.25 (d, 2 H, J = 9.5 Hz), 3.93 (s, 1 H), 2.10 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 199.9, 156.4, 136.8, 128.9, 125.8, 125.8, 54.9, 9.6; IR (CH_2Cl_2) 1700 (s), 1688 (s) cm^{-1}; MS (EI) 268 (M+, 100), 225 (13), 197 (14), 189 (15), 186 (44), 173 (18), 158 (44), 89 (11), 54 (22), 53 (14); HRMS calcd for $C_{14}H_{11}F_30_2$ 268.0708, found 298.0711.

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